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ON ELECTRON TRANSPORT
IN METALS AND SOLIDS



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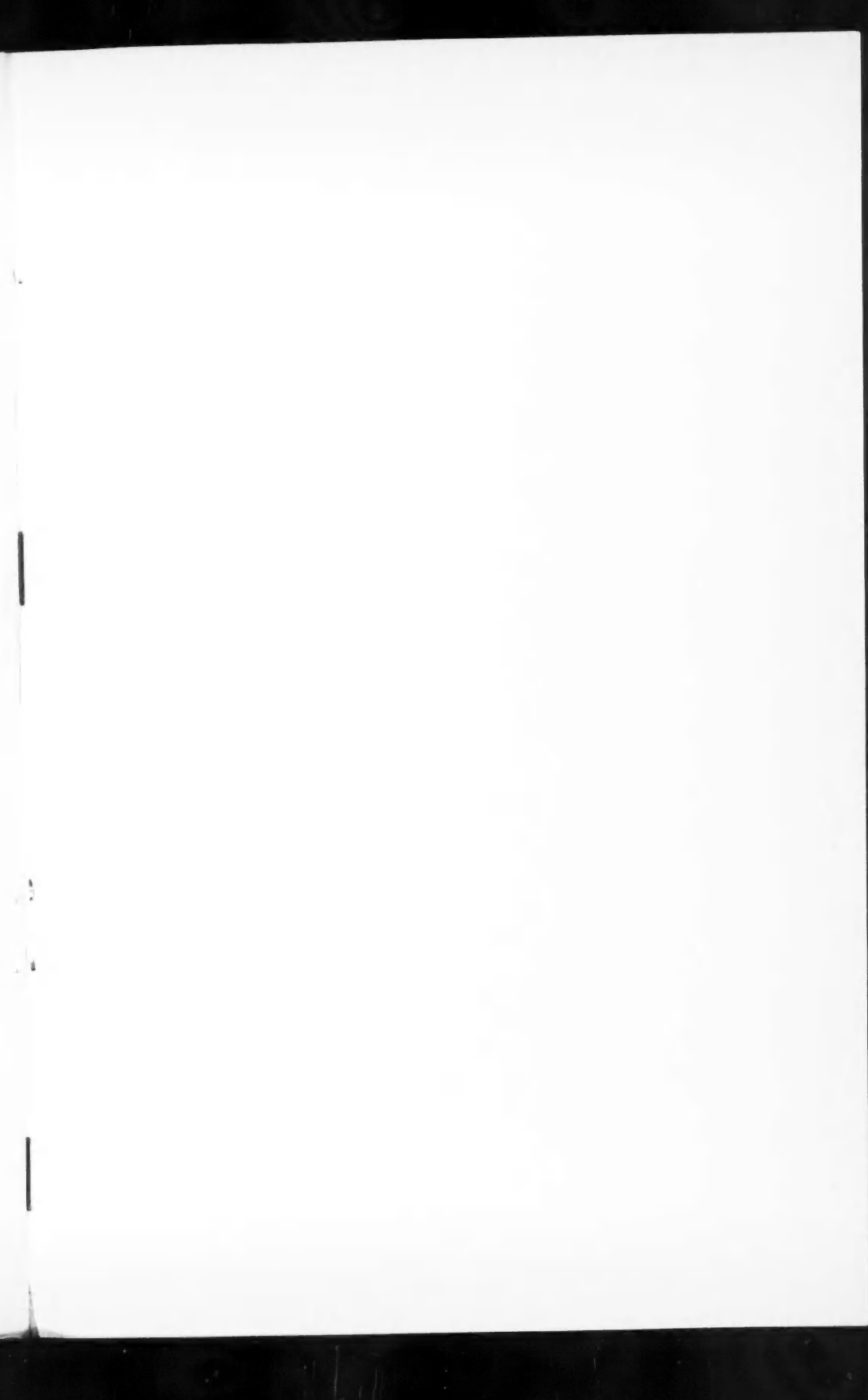
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FOREWORD

The papers in this special issue of the Canadian Journal of Physics are a record of an international conference on electron transport in metals and solids which was held in Ottawa at the National Research Laboratories from 10th to 14th September, 1956.

To ensure that an intimate atmosphere could be maintained with reasonably adequate time for discussion from the floor, the number of invitations sent out had to be strictly limited. On the lines of a Solvay Congress, or what is sometimes known as a "Working Conference", a few people were asked to present fairly comprehensive reviews of specific aspects of the field under study. Supplementary contributions were also received from some members of the Conference, and these are published here along with the reviews.

After some consideration and on the basis of past experience, it was decided that one member (Dr. T. H. K. Barron) would act as "Reporter" for the discussions following the papers presented. Written summaries of contributions were also welcomed, but not usually demanded, from those taking part in the discussions. We believe that rapidity of publication of these papers as a whole will appreciably enhance the value of the Conference, and nearly all proofreading has therefore been undertaken in Ottawa. Considerable care has been taken to ensure that manuscripts have been accurately printed and verbal contributions to the discussions fairly summarized and represented, but some omissions and inaccuracies will undoubtedly have occurred. We apologize in advance for these, and take full moral responsibility for them.

We should like here to thank Dr. Léo Marion, Editor-in-Chief of these Journals, Dr. Pauline Snure, Miss L. I. Ourom, and the other members of the Editorial Staff for their courtesy, kindness, and assistance in preparing this special issue. Miss L. Soublière and Mrs. D. Wayand have also been most helpful.

The Conference was sponsored and supported by the International Union of Pure and Applied Physics, U.N.E.S.C.O., and the National Research Council of Canada. The President of the Conference was Professor N. F. Mott, F.R.S.

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INTERACTION BETWEEN ELECTRONS AND LATTICE VIBRATIONS¹

By J. BARDEEN²

I. INTRODUCTION

In this review, we shall attempt to give a brief survey of progress made and problems encountered in calculating the interaction between electrons and lattice vibrations in crystals. We shall be concerned only with calculations from first principles and thus will not discuss methods for estimating interaction constants empirically from data on electrical or thermal conductivity. Some progress has been made on the following problems: (a) Monovalent metals. One of the main problems is how best to treat Coulomb interactions. The conduction electrons tend to shield the fields of the individual electrons as well as those of the ions. To treat this screening adequately, it is necessary to go beyond the individual particle picture, as discussed in the article of Pines (1) on electron-electron interactions. (b) Interaction of thermal velocity electrons and holes with non-polar modes in semiconductors and insulators. Since the relevant lattice vibrations have wave lengths large compared with the interatomic spacing, continuum methods involving a deformation potential can be employed. (c) Interaction with polar modes of long wave length. The interaction potential which results from the polarization associated with dilation can be determined from empirical constants of the crystal (dielectric constant, index of refraction, frequency of transverse modes). It is often necessary to take into account the polarization of the lattice resulting from the field of the electron as it moves through the crystal; the electron together with the associated polarization is known as a "polaron". Reasonably good solutions for the energies and mobilities have been obtained for both intermediate and strong coupling. Less progress has been made on conduction in *d*-band semiconductors (mostly oxides) and in impurity bands. The semiclassical picture of an electron hopping from site to site is probably closer than the quantum picture of an electron wave moving through the lattice and being infrequently scattered by thermal motion or imperfections. In this review, we will be concerned mostly with metals, but will give a brief account of the other problems.

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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II. METALS—CALCULATION OF ELECTRON-PHONON INTERACTION

According to the Bloch scheme (2), the individual electrons in a metal are described by functions $\psi_{\mathbf{k}}$, of wave vector \mathbf{k} , which are solutions of an equation of the form

$$(2.1) \quad \left(-\frac{\hbar^2}{2m} \nabla^2 + V_0 \right) \psi_{\mathbf{k}} = E_{\mathbf{k}} \psi_{\mathbf{k}},$$

where V_0 represents the periodic potential of the ideal crystal with ions in equilibrium positions. In general, V_0 might represent a linear operator and include exchange terms. As a result of lattice vibrations, V_0 is modified to

$$(2.2) \quad V = V_0 + \delta V.$$

Our main concern is the operator δV which causes transitions between the Bloch states.

Normal modes of the lattice may be designated by a wave vector κ and a polarization index σ . The number of different values of σ is equal to three times the number of atoms per unit cell. In a monatomic crystal with one atom per cell, the three values of σ correspond at long wave lengths to one longitudinal and two transverse waves. The displacement $\delta \mathbf{R}_j$ of an ion with equilibrium position \mathbf{R}_j^0 may be expanded in terms of the normal modes as follows†:

$$(2.3) \quad \delta \mathbf{R}_j = \mathbf{R}_j - \mathbf{R}_j^0 = (NM)^{-1} \sum_{\kappa, \sigma} q_{\kappa \sigma} \mathbf{e}_{\kappa \sigma} \exp(i\kappa \cdot \mathbf{R}_j^0),$$

where $\mathbf{e}_{\kappa \sigma} = \mathbf{e}_{-\kappa \sigma}^*$ represents the polarization of the mode κ, σ ($\sigma = 1, 2, 3$). Reality requires that $q_{\kappa \sigma} = q_{-\kappa \sigma}^*$. The angular frequency is $\omega_{\kappa \sigma}$ and the phonon energy $\hbar \omega_{\kappa \sigma}$. Matrix elements corresponding to emission and absorption of a phonon are:

$$(2.4a) \quad (q_{\kappa})_{N_{\kappa-1}, N_{\kappa}} = \left(\frac{\hbar N_{\kappa}}{2\omega_{\kappa}} \right)^{1/2} \quad (\text{absorption}),$$

$$(2.4b) \quad (q_{\kappa})_{N_{\kappa+1}, N_{\kappa}} = \left(\frac{\hbar (N_{\kappa} + 1)}{2\omega_{\kappa}} \right)^{1/2} \quad (\text{emission}).$$

The index σ has not been written explicitly. At high temperatures, $N_{\kappa} \simeq k_B T / \hbar \omega_{\kappa}$ and $q_{\kappa}^2 \simeq k_B T / \hbar \omega_{\kappa}^2$. Here k_B is Boltzmann's constant.

The scattering probability is usually calculated by time-dependent perturbation theory, with use of the Born approximation. This procedure appears to be justified for lattice scattering, although it is sometimes necessary to go beyond the Born approximation to give an adequate treatment of impurity scattering. The general expression for the probability per unit time that an electron be scattered from \mathbf{k} to \mathbf{k}' is

$$(2.5) \quad P(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} |M(\mathbf{k}, \mathbf{k}')|^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'} \mp \hbar \omega_{\kappa})$$

where

$$(2.6) \quad M(\mathbf{k}, \mathbf{k}') = \int \psi_{\mathbf{k}'}^* \delta V \psi_{\mathbf{k}} d\tau.$$

†Where the vector κ occurs as a subscript, it is written as κ for the convenience of the printer.

When an electron is scattered, a phonon is emitted or absorbed. The selection rule is

$$(2.7) \quad \mathbf{k}' = \mathbf{k} \pm \boldsymbol{\kappa} + \mathbf{K}_n$$

where \mathbf{K}_n is a lattice vector of the reciprocal lattice space. The upper signs in (2.5) and (2.7) correspond to absorption, the lower to emission, of a phonon of wave vector q .

Note that according to (2.7), $\boldsymbol{\kappa}$ and \mathbf{K}_n are determined uniquely for any given initial and final states, \mathbf{k} and \mathbf{k}' . If the vector difference $\mathbf{k} - \mathbf{k}'$ lies within the first Brillouin zone, $\mathbf{K}_n = 0$. This corresponds to normal scattering. If the difference lies outside of the first zone, $\mathbf{K}_n \neq 0$, and the scattering is called, after Peierls (3), an "Umklapp" process.

In calculating the conductivity, changes in the distribution function produced by the field and by scattering are treated as independent and the steady-state distribution is obtained from the solution of the appropriate Boltzmann equation. In other words, the scattering probability is assumed independent of field. Justification for the procedure, even when the electric field is very large, has been given by Bardeen and Shockley (4). They considered transitions between the time-dependent Bloch functions appropriate to a uniform applied electric field, F . These functions, originally discussed by Houston (5), correspond to states in which the momenta increase uniformly with time. Although the details of the transition processes may differ in large and small fields, the final expressions for the scattering probabilities are the same.

An alternative method to the use of the Boltzmann equation, and one which has not been explored very much, is to first consider the nature of the exact eigenfunctions and statistical distributions in the absence of a field. The effect of an applied field of frequency ν is then determined by use of dispersion theory. This method has been applied with some success to elastic scattering (6), but not, as far as the author is aware, to thermal scattering. It has advantages when τ (τ = mean time between collisions) is so small that difficulties with the uncertainty principle arise in the usual treatments.

We turn now to our main task of determining the interaction potential, δV . Consistent with the individual particle scheme, one might hope to calculate the wave functions by a Hartree-Fock self-consistent field procedure. With use of the Born-Oppenheimer approximation, a similar calculation could be made for a crystal distorted by a lattice wave. The difference in self-consistent field between the distorted and ideal crystals would then give the interaction potential, δV . The author has, in fact, applied this method to monovalent metals, using the Hartree rather than the Hartree-Fock approximation. Reasonably good results were obtained, but inclusion of exchange terms, particularly for treatment of interaction with phonons of long wave length, would be misleading. The difficulty is that the screening of the Coulomb fields of the electrons and ions is not properly taken into account in the Hartree-Fock scheme. It is well known that exchange terms coming from the long range part of the Coulomb interaction lead to difficulties in other problems in the theory

of metals as well. Because of screening, there is in fact no long range interaction between the individual electrons. As shown by the Bohm-Pines collective model, the screening radius is of the order of the inter-particle spacing, and about what one would estimate from a Fermi-Thomas model. The collective model yields an electron-phonon interaction equivalent at long waves to that obtained from the Hartree self-consistent field procedure, neglecting exchange. Before discussing these theories, we shall review some of the earlier attempts which lead to nearly equivalent results.

In the first calculations of conductivity of metals, Houston (7) and later Nordheim (7) assumed that the ions are shielded by the conduction electrons with a screening radius estimated from the Fermi-Thomas model, and neglected interactions between the conduction electrons themselves. They assumed that the total potential is given by a sum of the potentials of the screened ions:

$$(2.8) \quad V(\mathbf{r}) = \sum_j v_s(\mathbf{r}-\mathbf{R}_j),$$

where at large distances from the ion v_s has the asymptotic form

$$(2.9) \quad v_s(r) \sim -\frac{Ze^2}{r} e^{-\alpha r}.$$

The Fermi-Thomas expression for α is

$$(2.10) \quad \alpha^2 = \frac{4me^2}{\hbar^2} \left(\frac{3N}{\pi} \right)^{1/3}$$

where N is the concentration of conduction electrons. If the ions are displaced by $\delta\mathbf{R}_j$ from their equilibrium positions \mathbf{R}_j^0 , the change in potential is

$$(2.11) \quad \delta V = - \sum_j \delta\mathbf{R}_j \cdot \nabla v_s(\mathbf{r}-\mathbf{R}_j^0).$$

The scattering matrix element, obtained by substituting (2.3) into (2.11) and the result into (2.6), is

$$(2.12) \quad M(\mathbf{k}, \mathbf{k}') = -(NM)^{-1} q_{\kappa} \int_{\text{all space}} \psi_{\mathbf{k}'}^* (\mathbf{e}_{\kappa} \cdot \nabla v_s) \psi_{\mathbf{k}} d\tau,$$

where κ is the wave vector which satisfies the selection rule (2.7).

Mott and Jones (8) made use of the approximation of Wigner and Seitz that when an electron is in a given s -sphere it sees the potential only of the ion in the center of the sphere. This amounts to assuming a sharp cutoff or screening at the boundary of the sphere. If $v(r)$ is the unscreened field of the ion, the matrix element is

$$(2.13) \quad M(\mathbf{k}, \mathbf{k}') = -(NM)^{-1} q_{\kappa} \int_{s\text{-sphere}} \psi_{\mathbf{k}'}^* (\mathbf{e}_{\kappa} \cdot \nabla v) \psi_{\mathbf{k}} d\tau.$$

Jones (9) has recently extended this theory and compared results with other methods.

In the self-consistent field method (10), it is assumed that V is the sum of the unscreened field of the ions, V^i , and the Coulomb field of the conduction electrons, V^e . Thus

$$(2.14) \quad \delta V = \delta V^i + \delta V^e.$$

The perturbation δV causes a change $\delta\psi_k$ in the wave function of an electron. If the perturbed function is expanded in a series of unperturbed functions, we have

$$(2.15) \quad \delta\psi_k = \sum_{k'} b_{kk'} \psi_{k'}.$$

Terms in the sum which correspond to actual transitions, with conservation of energy, must be excluded. Poisson's equation is used to relate δV and the charge density associated with the perturbed wave functions, and this gives a relation between δV and δV^i . The ions are assumed to move more rigidly under the lattice deformation, so that the matrix elements of δV^i are given by an expression of the form (2.12) with v_s replaced by the unshielded ion potential v . A straightforward but somewhat lengthy calculation gives (see Reference 10)

$$(2.16) \quad \delta V_{kk'}^e = - \frac{\delta V_{kk'}^i}{1 + \frac{|\mathbf{k}-\mathbf{k}'|^2 W(|\mathbf{k}-\mathbf{k}'|)}{8\pi N e^2}},$$

where $W(\kappa)$ has the dimensions of an energy and is given by

$$(2.17) \quad W(\kappa) = \frac{2\hbar^2 k_0^2}{3m} \left\{ \frac{1}{2} + \frac{4k_0^2 - \kappa^2}{8k_0\kappa} \log \frac{2k_0 + \kappa}{2k_0 - \kappa} \right\}^{-1},$$

in which k_0 is the magnitude of the wave vector for the Fermi surface, assumed spherical. In calculating the charge density and potential of the conduction electrons, it is assumed that the unperturbed wave functions are nearly the same as those of free electrons. This assumption is most nearly valid for metallic sodium.

Nearly the same screening factor can be obtained more simply by use of the Fermi-Thomas method (11). Let E_F be the energy from the bottom of the conduction band to the Fermi level in the unperturbed metal. If the energy of the bottom of the band varies by δV while the Fermi level remains fixed, the relative change in electron density is

$$(2.18) \quad \frac{\delta N}{N} = \frac{(E_F - \delta V)^{3/2}}{E_F^{3/2}} = -\frac{3}{2} \frac{\delta V}{E_F}.$$

Poisson's equation, $\nabla^2 \delta V = 4\pi e^2 \delta N$, then gives

$$(2.19) \quad \delta V_{kk'}^e = - \frac{\delta V_{kk'}^i}{1 + \frac{|\mathbf{k}-\mathbf{k}'|^2 E_F}{6\pi N e^2}}.$$

This expression is identical with (2.16) if the bracket, $\{ \}$, in (2.17) is replaced by unity. The difference in $\delta V_{kk'}$ for the two expressions vanishes in the limit $\kappa \rightarrow 0$ and is only about 15% when $\kappa = k_0$. This gives justification for use of the Fermi-Thomas method in approximate calculations.

Bloch (12) has used the assumption of a "deformable" potential. If $V_0(\mathbf{r})$ is the potential in the ideal crystal, the potential in a crystal subject to the distortion $\delta\mathbf{R}$ is taken to be

$$(2.20) \quad \delta V(\mathbf{r}) = V_0(\mathbf{r} - \delta\mathbf{R}) - V_0(\mathbf{r}),$$

where $\delta\mathbf{R}$ is calculated at an arbitrary position \mathbf{r} by use of (2.3) with \mathbf{R}_j^0 replaced by \mathbf{r} . As one might expect, this hypothesis leads to an electron-phonon interaction of the correct order of magnitude, but it has no basic justification.

In actual calculations of the scattering matrix element, it is necessary to take the specific field of the ion into account. Use can be made of the following relation of Mott and Jones (8) which transforms a volume integral into a surface integral:

$$(2.21) \quad I = \int_{\text{cell}} \psi_{\mathbf{k}'}^* (\mathbf{e}_s \cdot \nabla V_0) \psi_{\mathbf{k}} d\tau = \frac{\hbar^2}{2m} \int_{\text{surface of cell}} \left(\psi_{\mathbf{k}'}^* \frac{\partial}{\partial n} \nabla \psi_{\mathbf{k}} - \nabla \psi_{\mathbf{k}} \frac{\partial}{\partial n} \psi_{\mathbf{k}'} \right) dS.$$

The integration is over a unit cell, which is most conveniently taken as the Wigner-Seitz polyhedron, nearly equivalent to the s -sphere. This transformation is particularly valuable for use with the quantum defect method.

In the Mott-Jones method, V_0 is just the potential, $v(r)$, of the unshielded ion in the center of the cell. If the further approximations are made that $\psi_{\mathbf{k}} = \exp(i\mathbf{k} \cdot \mathbf{r}) u_0(\mathbf{r})$ and $(du_0/dr)_{r=r_s} = 0$, it is found that

$$(2.22) \quad I = i\mathbf{e}_s \cdot (\mathbf{k} - \mathbf{k}') \frac{(v(r_s) - E_0)}{N} \left\{ \frac{3(\sin x - x \cos x)}{x^3} \right\} v_0(r_s)^2,$$

where

$$(2.23) \quad x = |\mathbf{k} - \mathbf{k}'| r_s = 2k_0 r_s \sin(\theta/2)$$

and θ is the angle between \mathbf{k} and \mathbf{k}' . The energy E_0 is the energy of the lowest Bloch state in the Wigner-Seitz approximation. The integral I is just that required for the calculation of the matrix element (2.13).

In the self-consistent field method (10), the potential V_0' is the potential of the ion in the center of the cell plus the potential of the charge distribution of the conduction electrons, which may be taken approximately that of a uniform charge cloud:

$$(2.24) \quad V_0'(r) = v(r) + \frac{e^2 r^2}{2r_s^3} - \frac{3e^2}{2r_s}.$$

The energy E_0' of the ground state is higher than the Wigner-Seitz energy, E_0 , by approximately $1.2 e^2/r_s$, so that

$$(2.25) \quad V_0'(r_s) - E_0' = v_0(r_s) - E_0 - 0.2e^2/r_s.$$

To calculate the contribution of the ions, the integral for the matrix element $\delta V_{\mathbf{k}\mathbf{k}'}^i$ may be divided into two parts, one over the central cell and the other over the remainder of space:

$$(2.26) \quad I = I_1 + I_2,$$

where

$$(2.27a) \quad I_1 = \int_{|\mathbf{r}| < r_s} \psi_{\mathbf{k}'}^* (\mathbf{e}_s \cdot \nabla v) \psi_{\mathbf{k}} d\tau,$$

$$(2.27b) \quad I_2 = \int_{|\mathbf{r}| > r_s} \psi_{\mathbf{k}'}^* (\mathbf{e}_s \cdot \nabla v) \psi_{\mathbf{k}} d\tau.$$

To evaluate I_1 , use can be made of (2.21) together with an explicit evaluation of the Coulomb terms. In I_2 , v may be replaced by $-e^2/r$ and the wave functions by plane waves. The sum of the two contributions is

$$(2.28) \quad I = i\mathbf{e}_s \cdot (\mathbf{k} - \mathbf{k}') \left(\frac{4\pi e^2}{|\mathbf{k} - \mathbf{k}'|^2} + \frac{V_0'(r_s) - E_0'}{N} \right) \left(\frac{3(\sin x - x \cos x)}{x^3} \right) v_0(r_s)^2.$$

In comparing (2.22) and (2.28), it must be remembered that (2.28) represents only the field of the ions, δV^i , and that when the contribution of the electrons is added in, the matrix element is reduced by a factor

$$(2.29) \quad \frac{\delta V_{\mathbf{k}\mathbf{k}'}^i + \delta V_{\mathbf{k}\mathbf{k}'}^e}{\delta V_{\mathbf{k}\mathbf{k}'}^i} = \frac{1}{1 + \frac{8\pi N e^2}{|\mathbf{k} - \mathbf{k}'|^2 W}}.$$

Jones (9) has given a comparison of the two methods for sodium. The approximation that the wave functions are similar to those of plane waves throughout most of the volume should be most nearly valid for this metal. He finds that the self-consistent field method gives somewhat larger scattering, particularly for small values of $|\mathbf{k} - \mathbf{k}'|$.

It is the rigid-ion model with shielded ions which is probably most easy to apply when there is more than one valence electron per atom and when plane wave approximations for the electrons are not satisfactory. As yet, however, no detailed calculations have been attempted for any but the monovalent metals. For these, the model yields results similar to those of the self-consistent field method.

From a fundamental point of view, the most satisfactory method for treating the Coulomb interaction between electrons is the collective model of Bohm and Pines (13). As discussed by Pines (1), the long-range part of the Coulomb interaction leads to coherent plasma oscillations of the electron gas. When coordinates for these are introduced and separated out in the Hamiltonian, one is left with a short-range screened interaction between the individual electrons. This model has been extended to include ionic motion by Bardeen and Pines (14). The coupled motion of electrons and ions leads to high frequency plasma modes and to low frequency acoustic modes. Interaction of the individual electrons with the acoustic modes is essentially equivalent to that given by the self-consistent field method, neglecting exchange. Another consequence of the theory is an expression for the sound-wave frequency in terms of the matrix elements of the electron-phonon interaction. A numerical calculation (14) for the velocity of sound in metallic sodium in the long wave limit agrees with experimental values and provides an additional check on the method.

Plasma modes are introduced only for wave vectors $|\kappa| < \kappa_c$, where κ_c is somewhat less than the radius of the Fermi surface, k_0 , in monovalent metals. For shorter waves, the most satisfactory treatment is probably one given by Nakajima (15), which is nearly equivalent to the self-consistent field method. We shall first give the results of the Nakajima method and then those of the collective electron model.

Bloch functions are introduced which correspond to motion of electrons with the ions in equilibrium positions in a uniform sea of negative charge. Let $c_{\mathbf{k}}^*$ and $c_{\mathbf{k}}$ be creation and destruction operators for electrons in states of energy $E_{\mathbf{k}}$, designated by the wave vector \mathbf{k} . These operators are assumed to obey the commutation relations of Fermi-Dirac statistics. For simplicity we shall omit the spin index which would be required for a complete designation of the state. Further, let Ω_{κ} and v_{κ}^i be the longitudinal vibrational frequency and electron-phonon interaction parameter in the absence of electron motion and ω_{κ} and v_{κ} the true values for these quantities when electron motion is included. The Hamiltonian may then be expressed in the form (see Reference 15)

$$(2.30) \quad H = \sum_{\mathbf{k}} E_{\mathbf{k}} c_{\mathbf{k}}^* c_{\mathbf{k}} + \frac{1}{2} \sum_{\kappa} (\rho_{\kappa}^* \rho_{\kappa} + \omega_{\kappa}^2 q_{\kappa}^* q_{\kappa}) + \sum_{\kappa} v_{\kappa} q_{\kappa} \rho_{-\kappa} \\ + 2\pi e^2 \sum_{\kappa} \frac{\rho_{\kappa} \rho_{-\kappa}}{\kappa^2} + \sum_{\kappa} (v_{\kappa}^i - v_{\kappa}) q_{\kappa} \rho_{-\kappa} + \frac{1}{2} \sum_{\kappa} (\Omega_{\kappa}^2 - \omega_{\kappa}^2) q_{\kappa}^* q_{\kappa},$$

where ρ_{κ} is a Fourier component of the density matrix:

$$\rho_{\kappa} = \sum_{\mathbf{k}} c_{\mathbf{k}-\kappa}^* c_{\mathbf{k}}; \quad \rho_{-\kappa} = \sum_{\mathbf{k}} c_{\mathbf{k}}^* c_{\mathbf{k}-\kappa}.$$

The first term in the second line of (2.30) represents the Coulomb interaction between electrons. A plane wave approximation has been used to determine the coefficient, $2\pi e^2/\kappa^2$. For simplicity we have omitted the polarization index for the vibrational coordinates. Frequencies of transverse modes are to a first approximation independent of electron motion, but they would be affected some by Umklapp processes. Such processes could be included in the above formalism by allowing the sum over κ in the electron-phonon interaction to run out of the first Brillouin zone and by supposing that q_{κ} then represents the vibrational amplitude corresponding to the reduced wave vector.

The values of ω_{κ} and v_{κ} are determined as follows. A canonical transformation (16) is made to eliminate the linear term in q_{κ} in the first line of (2.30). If S represents the generating function for this transformation, the transformed Hamiltonian to the second order is

$$(2.31) \quad H' = H + i\hbar^{-1}[H, S] - \frac{1}{2}\hbar^{-2}[[H, S], S] + \dots$$

The interaction parameter v_{κ} is chosen so as to eliminate the linear term in q_{κ} in the second line, and finally ω_{κ} is chosen so that there are no diagonal terms in $q_{\kappa}^* q_{\kappa}$ to the second order in the transformed Hamiltonian. In making the transformation, linear terms in q_{κ} are treated as first order and the last term, with $\Omega_{\kappa}^2 - \omega_{\kappa}^2$ as a factor, as second order in the original Hamiltonian.

Nakajima (15) omitted exchange terms in the commutator, $[\rho_{-\kappa} \rho_{\kappa}, S]$, of the Coulomb interaction. This makes the analysis essentially equivalent to

the Hartree rather than the Hartree-Fock self-consistent field method. One effect of exchange is to simply add an exchange energy to the energy, E_k , of the individual electron in the final expression. However, there are other exchange terms which cannot be treated so simply. A brief discussion of the effects of exchange is given in the paper of Bardeen and Pines (14).

The expressions obtained by Nakajima for v_k and ω_k , omitting exchange, are given by

$$(2.32) \quad v_k^p = v_k - v_k^i = -\frac{4\pi e^2}{\kappa^2} \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k} - \mathbf{\kappa})}{E_{\mathbf{k}-\mathbf{\kappa}} - E_{\mathbf{k}} + \hbar\omega_k},$$

and

$$(2.33) \quad \Omega_k^2 - \omega_k^2 = v_k^i v_k \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k} - \mathbf{\kappa})}{E_{\mathbf{k}-\mathbf{\kappa}} - E_{\mathbf{k}} + \hbar\omega_k} = -\frac{\kappa^2}{4\pi e^2} v_k^i v_k^p.$$

The expression for v_k^p is essentially the same as that given by the author by the Hartree self-consistent field method, and that for ω_k the same as one derived by Toya (17), also using this method (18). The sums over \mathbf{k} should also include sums over the two spin values. Umklapp terms have been neglected in (2.33).

The introduction of variables $Q_{\mathbf{\kappa}}$, $P_{\mathbf{\kappa}}$, for $|\mathbf{\kappa}| < \kappa_c$, representing plasma oscillations, is identical with the procedure used in the absence of ion motion (13). Additional terms

$$(2.34) \quad H_{\text{add}} = \frac{1}{2} \sum_{|\mathbf{\kappa}| < \kappa_c} P_{\mathbf{\kappa}}^* P_{\mathbf{\kappa}} - i \sum_{|\mathbf{\kappa}| < \kappa_c} \left(\frac{4\pi e^2}{\kappa^2} \right)^{\frac{1}{2}} P_{\mathbf{\kappa}} \rho_{\mathbf{\kappa}}$$

are added to the Hamiltonian, and the system wave function is required to satisfy a set of subsidiary conditions:

$$(2.35) \quad P_{\mathbf{\kappa}} \Psi = 0.$$

If these conditions are satisfied exactly, H_{add} contributes nothing to the energy. In practice, H_{add} is used to simplify the Hamiltonian and to isolate the plasma oscillations; the subsidiary conditions are satisfied only approximately. Justification for this procedure is based on a variational argument (13).

A series of canonical transformations is used to eliminate from the Hamiltonian as nearly as possible interaction terms between the individual electrons, plasma oscillations, and phonons. It is further required that there be no coupling of the electrons and phonons via the subsidiary conditions. The term $\frac{1}{2} \sum (\Omega_k^2 - \omega_k^2) q_{\mathbf{k}}^* q_{\mathbf{k}}$ in the second line of (2.30) is again treated as of second order in the original Hamiltonian and ω_k chosen so as to eliminate diagonal terms in $q_{\mathbf{k}}^* q_{\mathbf{k}}$ to the second order in the transformed Hamiltonian. It is found that the shielded interaction constant is given by an expression identical with (2.32). Terms which remain to the second order after the canonical transformations are of the form:

$$(2.36) \quad H = H_0 + H_{e1-p1} + H_{eh.Coul.} + H_2,$$

where H_0 is the Hamiltonian for non-interacting electrons, phonons, and plasma oscillations, H_{e1-p1} is a small residual electron-plasma interaction, $H_{eh.Coul.}$ is a shielded Coulomb interaction between the individual electrons,

and H_2 is an interaction between electrons resulting from the electron-phonon interaction:

$$(2.37) \quad H_2 = \sum_{|\mathbf{k}| < \kappa_c} v_{-\mathbf{k}} \rho_{\mathbf{k}} c_{\mathbf{k}-\mathbf{k}}^* g(\mathbf{k}, \mathbf{k}) + \sum_{|\mathbf{k}| > \kappa_c} v_{-\mathbf{k}} \rho_{\mathbf{k}} c_{\mathbf{k}}^* c_{\mathbf{k}-\mathbf{k}} g(\mathbf{k}, \mathbf{k}).$$

Here

$$(2.38) \quad g(\mathbf{k}, \mathbf{k}) = -\frac{\hbar^2 v_{\mathbf{k}}}{(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{k}})^2 - \hbar^2 \omega_{\mathbf{k}}^2}.$$

A vanishing energy denominator in (2.38) corresponds to the possibility of real rather than virtual transitions of the electrons, and such terms must be omitted in the canonical transformation. Terms with small energy denominators contribute a negligible amount to the electron-phonon interaction constant and to the vibrational frequencies. The sums over vanishing energy denominators in (2.32) and (2.33) should be taken by principal parts.

It is the interaction H_2 which is believed to be responsible for superconductivity. The important terms are those for which $(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{k}})^2 < \hbar^2 \omega_{\mathbf{k}}^2$. When the electron-phonon interaction is sufficiently strong (and this gives a criterion for superconductivity) such terms can not be treated by perturbation theoretic methods, and so can have a marked effect on the system wave function. No satisfactory solution to the problem for intermediate or strong coupling has yet been given.

We may summarize the results of this section as follows. The Hartree self-consistent field method is probably satisfactory for the calculation of electron-phonon interactions in the long wave limit. Coulomb interactions between electrons have so far been treated with a plane wave approximation for the valence electrons. This is probably satisfactory only for sodium and perhaps a few other alkali metals. The method probably gives only the correct order of magnitude for short waves and Umklapp processes. A more exact theory would require a better treatment of exchange terms. In view of these difficulties, perhaps the simplest and most reliable method to estimate electron-phonon interactions in more complicated cases is to use the rigid-ion model with an appropriately screened electron-ion interaction, and to neglect the specific interaction between electrons.

III. APPLICATIONS TO ELECTRICAL CONDUCTIVITY—IMPORTANCE OF UMKLAPP PROCESSES

That Umklapp processes (U-processes) contribute a substantial part of the high-temperature resistivity of monovalent metals has been known for a long time (10). It has been only recently that it has been recognized that such processes are very important at low temperatures as well.

Since the first Brillouin zone in a monovalent metal can accommodate two valence electrons per atom, the radius of the zone boundary which gives the maximum wave vector, κ_D , of the Debye spectrum is approximately $2^{1/2}$ times the radius of the Fermi surface, k_0 . This means that all transitions through angles greater than about $2 \sin^{-1/2-2/3}$ ($\sim 79^\circ$) take place through U-processes.

Expressions for the matrix elements, such as (2.12) or (2.13), apply to

U-processes as well as to normal processes. To a first approximation, the matrix elements are of the form

$$(3.1) \quad M(\mathbf{k}, \mathbf{k}') = q_{\kappa} \epsilon_{\kappa} \cdot (\mathbf{k} - \mathbf{k}') f(|\mathbf{k} - \mathbf{k}'|).$$

For normal processes, $\kappa = \pm(\mathbf{k} - \mathbf{k}')$, and thus only the longitudinal component (ϵ_{κ} parallel to κ) contributes to the scattering. Transverse phonons contribute as well to U-processes, and in fact give more than half of the resistance.

At high temperatures ($T > \Theta_D$),

$$(3.2) \quad \overline{q_{\kappa}^2} = k_B T / 2\omega_{\kappa}^2.$$

Thus, the scattering probability is of the form

$$(3.3) \quad P(\mathbf{k}, \mathbf{k}') \sim \frac{(\epsilon_{\kappa} \cdot (\mathbf{k} - \mathbf{k}'))^2}{\omega_{\kappa}^2} f(|\mathbf{k} - \mathbf{k}'|).$$

For normal processes, with the Debye theory, the first factor is a constant, so that the probability depends only on the angle between \mathbf{k} and \mathbf{k}' and not on the orientation of \mathbf{k} and \mathbf{k}' relative to the crystal axes. This is not true of U-processes. The author, in the 1937 paper (10), assumed for simplicity that $|\kappa| = \kappa_D$ for all U-processes. This assumption gives a scattering independent of orientation, but considerably underestimates U-scattering, since κ may be considerably less than κ_D for many of them. A much improved treatment has recently been given by Jones (9).

The importance of U-processes at low temperatures was first pointed out by Ziman (19), who used (2.28) as well as a semiempirical scattering probability. He was able to get an improved agreement with experimental values of electrical and thermal conductivities for Na in the temperature range $T > 10^\circ \text{K}$. if he assumed a forward scattering lobe stronger and narrower and a backward scattering (U-processes) larger than given by (2.28). The latter would follow from an improved treatment of U-processes, as pointed out by Jones (9).

Because of the rapid temperature variation of the number of phonons with energy when $\hbar\omega > k_B T$, transport properties at very low temperatures are particularly sensitive to the details of the scattering mechanism. In addition to a more adequate treatment of U-processes, it is necessary to use a more accurate vibrational spectrum than is given by the Debye theory, and to take into account the deviations of the Fermi surface from a sphere. As pointed out by Ziman (20), the Kohler variational method provides a convenient and accurate method for calculating transport properties, even when the scattering is a complicated function of angle.

Calculations of this sort have been made by Bailyn and Brooks (21) on the alkali metals. Only a brief account of this work has been presented up to the time of the writing of the present review. The self-consistent field method was used to determine the scattering probabilities. The vibrational spectrum was estimated from the elastic constants and an empirical dispersion factor. They report that improved calculations based on the Born-von Karman model are in progress. So far, an effective mass approximation with spherical energy surfaces has been used, but corrections will be made in the final calculations.

Perhaps the most surprising conclusion of this work is that U-processes dominate the scattering down to the lowest temperatures at which the thermal resistivity can be observed ($\sim 1^\circ \text{K.}$). Since transverse modes have considerably lower frequencies than longitudinal, they give nearly all of the scattering at low temperatures. Theoretical resistivities of the correct order of magnitude over the complete temperature range were obtained for Na, K, Rb, and Cs. Except for Li, the temperature dependence at very low temperatures is in agreement with measurements of MacDonald and Mendelssohn (22) and of MacDonald, White, and Woods (23).

Since the U-processes which dominate the scattering at low temperatures do not conserve wave vector, there is no difficulty with the so-called Peierls paradox concerning the thermal equilibrium of the phonon distribution.

IV. DEFORMATION POTENTIAL METHODS

At ordinary temperatures, electrons and holes in semiconductors and insulators have wave lengths ($\sim 10^{-6} \text{ cm.}$) large compared with atomic distances, and interact with acoustic waves of comparably long wave length. This suggests that the electron-phonon interaction can be determined by a continuum-type theory. One may expect the energy bands to move up and down with strain of the lattice. Bardeen and Shockley (24) have shown that such a variation in band edge due to a varying strain acts on an electron as a slowly varying electrostatic potential would, and can be treated in an effective mass approximation.

In the original formulation (24), it was assumed that the band position is determined solely by the local strain. This would not be true if there were polarization induced by the strain which gives an electrostatic potential acting over large distances. It also would not be true in metals where the conduction electrons would tend to flow in to shield the direct variation induced by deformation (25). However, it is probably a good approximation in non-polar crystals such as Ge or Si, for which most applications of the method have been made. Variations in electrostatic potential could be included if present.

The general expression for the energy of an electron with wave vector \mathbf{k} in a crystal subject to a homogeneous strain ϵ_{ij} is

$$(4.1) \quad E(\mathbf{k}) = E_0(\mathbf{k}) + \sum_{ij} E_{ij} \epsilon_{ij} + \sum_{ijlm} E_{ijlm} k_i k_m$$

where \mathbf{k} is measured from the energy minimum in both the undeformed and deformed crystals. The second term gives the shift in the band edge and the third arises from a change in effective mass. While both terms may contribute to the scattering, the former usually dominates.

When the energy surfaces are spherical, the shift in band edge is determined solely by the dilation. As is the case for Ge and Si, the bands may be degenerate and have a lower symmetry than the crystal itself. In this case, shear waves are important, as pointed out by Herring and Vogt (26) and by Dumke (27), who have worked out the general theory for multi-valley energy bands. Information about the interaction constants, E_{ij} , can be obtained from elasto-resistance data on homogeneously deformed specimens.

Interaction of electrons with the upper branch of the vibrational spectrum of crystals such as Ge or Si (usually called optical modes, in analogy with the corresponding vibrations in polar crystals) can be important (28). It is difficult to estimate the interaction constant from first principles. The problem has been discussed recently by Ehrenreich and Overhauser (29) and by Harrison (30).

V. INTERACTION WITH POLAR MODES—THE POLARON PROBLEM

Since there exist excellent reviews of work on the polaron problem by Fröhlich (31) and by Haken (32), we shall give here only a very brief account of some of the conclusions. The main mathematical difficulty is to take into account the polarization of the lattice induced by the electron as it moves along. This can be interpreted as a field theoretic problem of the interaction of a particle with a field; the electron is accompanied by a cloud of virtual phonons. The problem is usually idealized so as to treat the induced polarization by continuum methods and to assume that all phonons have the same frequency. In other words, the atomic structure of the crystal is not taken into account. It is then one of the simplest cases of a particle interacting with a field that can be discussed, and as such has received considerable attention from field theorists. Reasonably good solutions for the energy and mobility of a polaron are now available for both intermediate and strong coupling.

As pointed out by Fröhlich, Pelzer, and Zienau (33), it is convenient to characterize the strength of the interaction between electrons and polar modes in a polar crystal by a dimensionless coupling constant,

$$(5.1) \quad \alpha = \frac{e^2}{2\hbar} \left(\frac{2m}{\hbar\omega} \right)^{1/2} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right),$$

where m is the effective mass for a stationary lattice, ω is the angular frequency of the polar modes, n is the index of refraction, and ϵ is the dielectric constant. When $\alpha < 1$, the mobility and energy of the polaron can be determined by perturbation theoretic methods.

The very strong coupling limit ($\alpha > 10$) can be treated in the adiabatic approximation, as has been done by Pekar (34) and by Markham and Seitz (35). In this case the picture of a "self-trapped" electron is a reasonable first approximation. The induced polarization forms a potential well in which the electron moves. The frequency of the electron in its orbit is large compared with ω , so that one can compute the induced polarization from the average charge density $-e\psi^*\psi$. The effective mass of such a polaron is large and the mobility low.

The actual range of coupling constants in ionic crystals is of the order of 3 to 6, so that neither the weak nor strong coupling theories are adequate. Solutions valid in this intermediate range were first obtained independently by Gurari (36) and by Lee, Low, and Pines (37). They find for the shift in energy of a slow electron

$$(5.2) \quad \Delta = -\alpha\hbar\omega$$

and for the effective mass

$$(5.3) \quad m^* = m(1 + \frac{1}{6}\alpha).$$

The value of ΔE is equivalent to that obtained by perturbation theory. The mobility, derived by Low and Pines (38), in the intermediate coupling range is

$$(5.4) \quad \mu = \frac{1}{2\alpha\omega} \left(\frac{e}{m} \right) \left(\frac{m}{m^*} \right)^3 f(\alpha) \left(\exp \frac{\hbar\omega}{k_B T} - 1 \right),$$

where $f(\alpha)$ varies slowly with α and is approximately 1.2 for $3 < \alpha < 6$. The perturbation theory limit corresponds to taking $f(\alpha) = 1$ and $m = m^*$. Thus, as suggested by Fröhlich *et al.* (33), values in the intermediate coupling range are much closer to those of perturbation theory than to the adiabatic limit. Feynman (39) has given a theory valid over the entire range of coupling constants.

VI. CONCLUDING REMARKS

Reasonably satisfactory methods are available for calculating electron-phonon interaction constants in the monovalent metals. They can probably be extended with some difficulty to polyvalent metals. The best starting point from a fundamental point of view is the Bohm-Pines collective model, but the rigid-ion approximation should give a good estimate.

To calculate transport properties at low temperatures, it is essential not only to include Umklapp processes, but to use a more accurate vibrational spectrum than is given by the Debye theory. It will probably also be necessary to have a fairly good knowledge of the shape of the Fermi surface.

Deformation potential methods for long waves in semiconductors can be used either to calculate interaction constants from first principles or to estimate them from measurements on homogeneously deformed crystals. The problems of estimating interactions with the optical branch, intervalley scattering, and scattering of high energy electrons in non-polar crystals are difficult, but some progress has been made.

An important theoretical problem is to calculate electron-lattice interaction energies and transport properties when the coupling is so large that it can not be treated by perturbation theory. Satisfactory solutions have been obtained only for the polaron problem. The solution of the corresponding problem in metals would very likely lead to a theory of superconductivity.

We have not discussed the possibility of a coupled motion of electrons and a traveling acoustic wave in which the electrons are carried along with the wave. On the basis of theoretical calculations, Parmenter (40) predicted that a unidirectional sound wave in a rod should produce an appreciable electric potential difference between the ends of the rod when no current is flowing. The mathematical theory has been developed further by Brillouin (41), who shows under what conditions an electron may be trapped in the potential minima and move with a wave. On the basis of a one-dimensional model, Fröhlich (42) suggested that coupled motions may play a role in superconductivity. As far as the writer is aware, no such effects have been observed, and it is as yet uncertain what role, if any, such motions play in transport phenomena or in superconductivity.

Little progress has been made on the problem of conduction in semiconductors with incomplete d -bands, in which the mobility of the carriers is very low. Perhaps the solution is to be found along the lines of the polaron problem in the strong coupling limit, but it would be essential to take the atomic structure of the material into account.

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DISCUSSION OF BARDEEN'S PAPER

Mott: Would Bardeen or anyone else like to say something about the effect of electron-electron collisions? Twenty years ago it was estimated (W. G. Baber, Proc. Roy. Soc. A, **158**, 383 (1937); Mott and Jones, p. 277) that this would give a contribution to the electrical resistance that varies as T^2 , which would be large when the effective mass is high. Is the theory right, and is there any experimental evidence?

Mendelssohn: In recent measurements at Oxford we have found a T^2 variation in palladium, but I shall be mentioning this in my paper for this Conference.

Fröhlich: The normal method for dealing with a displaced atom or an impurity is to take as the unperturbed Hamiltonian the Hamiltonian of the regular lattice, and the Bloch functions $\psi_k = u_k \exp(i\mathbf{k} \cdot \mathbf{r})$ as the unperturbed wave functions; the effect of the irregularity is taken as the perturbation. This is rather nasty, since the perturbation is not at all small near the actual lattice site—although of course there is the method of transformation to surface integrals devised by Mott and Jones.

I have found that it is possible to avoid this difficulty by modifying the unperturbed wave functions. For simplicity, suppose that the Bloch functions of the perfect lattice are

$$\psi_k = u \exp(i\mathbf{k} \cdot \mathbf{r})$$

where u is independent of \mathbf{k} . We redefine u for the displaced lattice in a way analogous to the Wigner-Seitz model, so that the function solves the Schrödinger equation in each Wigner-Seitz cell with suitable boundary conditions; this equation is *not* of the simple form $Hu = Eu$, but there is an additional term resulting from the displacement.

In this way we start with an unperturbed wave function much closer to the true wave function in the middle of the Wigner-Seitz cell.

Seeger: This may be a useful method for calculating the scattering effect of a stacking fault in close-packed crystals, where of course the displacement from a regular lattice is of the order of the lattice spacing.

Fröhlich: In semiconductors one could expect excitation of plasma oscillations to be considerable and to have then quite a severe effect upon the scattering. The density of conduction electrons is much lower than in metals, and hence the plasma frequency is lower also, so that $\hbar\omega_p$ could be comparable with kT .

White: In regard to the point raised by Professor Mott concerning electron-electron interaction, there does seem to be experimental evidence for a T^2 term in the ideal electrical resistance of some transition elements, which we have been studying recently both here and in Sydney. In the case of platinum,

our results agree with those of de Haas and de Boer showing a T^2 term which becomes important below about 10°K. ; and there are also other high purity elements, e.g. tungsten, where there is a suggestion in the experimental data that a T^2 term may be important at low temperatures. However in general the requirements of very high purity and suitable dimensions have not yet been sufficiently well met to give an answer for other transition metals. What the data do show is that whereas some of the transition metals such as palladium and chromium show an ideal electrical resistance which follows a $(T/\theta)^3 J_3(\theta/T)$ function (cf. Wilson) and hence at temperatures $\leq \theta/10$ fall as T^3 , others follow more closely a Bloch-Grüneisen law and fall almost as rapidly as T^3 at low temperatures; there are also others showing an intermediate behavior. Thus the evidence for the importance of s - d band transitions at low temperatures is rather uncertain.

I should like to ask Professor Bardeen his views on the question of electrons interacting with lattice vibrations of all polarizations. On the assumption of a perfectly spherical Fermi surface, only longitudinal waves should interact with free electrons, but in view of his recent work with Dr. Pines, is this likely to be the case in most metallic elements?

Bardeen: Even with a spherical Fermi surface, interaction with transverse phonons can occur through Umklapp processes. Baily and Brooks at Harvard have calculated that in the alkali metals Umklapp processes dominate the resistivity down to 1° or 2°K. , so that according to them transverse phonons are very important in this range.

Mott: Did they use a Debye vibrational spectrum or something better?

Bardeen: Something better.

Sondheimer: Ziman has considered Umklapp processes in sodium, as you mentioned in your report.

Pines: The Harvard work goes beyond this.

Ziman: Using Bardeen's formula for the scattering cross-section, the longitudinal Debye spectrum, and a spherical Fermi surface gives a resistivity ρ looking very much like ρ_s , but with a different value of θ . One must be careful not to overinterpret the fit even of a one-parameter theory.

Mendelssohn: What experimental evidence is there for believing that the longitudinal and transverse vibrational spectra make markedly different contributions to the scattering? Blackman made some calculations on this a few years ago, but found that the results disagreed with experiment.

Seeger: If Umklapp processes are so important, this should show up in the magnetoresistance, since Umklapp scattering is not isotropic even with a spherical Fermi surface; if the estimate that Umklapp scattering accounts for three-quarters of the resistance in sodium at helium temperatures is correct, it seems likely that it is responsible for most of the magnetoresistivity of monovalent metals. This suggestion implies that the magnetoresistivity (in the Kohler diagram) should be reduced considerably at temperatures low enough for Umklapp processes to become unimportant. This might be checked by experiment.

Moreover there should be a temperature effect: the magnetoresistance should fall off at low enough temperatures, when the Umklapp processes are frozen out.

Sondheimer: The ideal resistance is so small at these temperatures that measurements may be very difficult.

Bhatia: Even if Umklapp processes were neglected, a spherical Fermi surface would not ensure isotropy in the relaxation-time and magnetoresistance of an elastically anisotropic metal. Sodium is strongly elastically anisotropic.

MacDonald: May I enter a caveat at this point about the interpretation of magnetoresistance in metals? The theory assumes that the Lorentz force acting on the conduction electrons is, on the average, balanced by the Hall field, so that magnetoresistance is to be ascribed to a dispersion of electron velocities (non-spherical Fermi surface) and/or of electron relaxation times. A satisfactory detailed explanation of experimental data on metals is still lacking—there are in fact even *qualitative* aspects we do not yet understand—but in general terms we do find that the magnetoresistance of an “ideal” metal, such as sodium, is low while that of a metal like tungsten is high.

I believe that the conclusions presented above are broadly valid so long as l/R is smaller than unity (l is the electron mean free path and R the radius of a free conduction electron orbit in the applied magnetic field. In this case, it appears that the assumed balancing of Lorentz force and Hall field is quite acceptable, but that when $l/R \gtrsim 1$ we may have to inquire rather carefully into the validity of this assumption. Experiments on sodium with values of l/R up to something over 50 are in course of publication (MacDonald, Phil. Mag. and Bull. inst. intern. froid (Louvain Conference, 1956)); and with a Corbino disk of sodium (which is an extreme case where a Hall field *cannot* be established), Mr. P. C. Clapp in our group observed a magnetoresistance increase of about 250 in a magnetic field of about 20 kgauss. A corresponding specimen of sodium cast in a conventional capillary tube would show an increase of about a factor of 2.

Klemens: Returning to Dr. Mendelssohn's query whether there was any evidence for the assertion that transverse lattice waves interact as strongly as longitudinal waves, other than the magnitude of the θ -value from electrical resistance:

There is quite definite evidence that transverse waves interact as strongly, or nearly as strongly, as longitudinal waves with conduction electrons, from the magnitude of the lattice thermal conductivity. The lattice thermal conductivity is limited by the scattering of phonons by electrons: the intrinsic thermal resistivity is determined by the same processes, and the relationship between these two quantities is quite sensitive to the mode of coupling, differing by a factor of about 20 in these two cases. In the two metals studied so far, namely silver and copper, it appears that the interaction with transverse waves is as strong, or nearly as strong, as with longitudinal waves.

Gorter: I shall be describing later experiments at Leiden in which there appeared an anomaly in the thermal conductivity of silver alloys. The interpre-

tation of this seems to support the general ideas of Dr. Klemens, but casts some doubt on the equality of the two interactions discussed (cf. the discussions of the papers of Mendelssohn and White).

Bardeen: The self-consistent field approximation gave originally an estimate of the room temperature electrical resistance close to that observed. But a better treatment of the effect of Umklapp processes would give too high a theoretical value.

Ziman: How does Professor Bardeen feel about theoretical interactions for Umklapp processes?

Bardeen: None of the theories are very satisfactory, since they are reasonable approximations only for long wavelengths. Umklapp processes are perhaps best treated by using the rigid-ion approximation with a Thomas-Fermi screening factor. The Bohm-Pines treatment is very difficult for these wavelengths, and all one can say is that it gives results for long wavelengths agreeing with the rigid-ion approximation.

Klemens: So long as the interaction is sufficiently strong to provide a "short circuit" across the Fermi surface, it doesn't matter what its exact value is.

Kubo: The effect reported now by Dr. MacDonald in connection with the magnetoresistance is extremely strange. It is very hard to find any reason for a serious breakdown of the existent theory by the condition he just mentioned: that is, $l/R \gtrsim 1$, or in other words $\omega_0 \tau \gtrsim 1$, where ω_0 is the angular frequency of the electrons and τ the relaxation time. The quantum mechanical effect is of course to be considered, but it becomes important only when the magnetic field is so high that the separation of quantized level by the magnetic field becomes comparable to the average kinetic energy of the electron. This magnetic field is extremely large for ordinary metals. There exists in some solids a quantum mechanical effect which shows up in an oscillatory behavior of magnetoresistance, Hall effect, and other properties; but this effect is not to be seen in ordinary metals. Incidentally, we have recently studied theoretically these quantum mechanical effects and were able to develop a theory which can be applied in particular to those metals such as bismuth which show these effects, and can be used to analyze the oscillations of transport properties with the increase of magnetic field.

Chambers: I have a further warning about the interpretation of magnetoresistance measurements. Until we understand why it is that over a wide range of field the magnetoresistance is proportional to H , instead of being either proportional to H^2 or constant (in the high field region), we cannot expect to interpret the results of our measurements in any reliable way.

ON SOME ELECTRICAL AND MAGNETIC PROPERTIES OF METALLIC SOLID SOLUTIONS¹

By J. FRIEDEL²

ABSTRACT

The resistivity, thermoelectric power, and magnetic susceptibility of metallic solid solutions at room temperature are reviewed, and their relation with their electronic structure emphasized. The special properties of transitional impurities are related to the emptying of their d shells.

INTRODUCTION

The purpose of this paper is to review some characteristic electrical and magnetic properties of metallic solid solutions in relation to their electronic structure. The emphasis will be on the peculiar properties of transitional impurities like Ni, Co, Fe, Mn, Cr, in ordinary metals like Cu or Al, which will be related to a partial emptying of their d shell. The more regular properties of alloys with nontransitional constituents will be first recalled.

The properties studied here are those most easily related to the electronic structure: room or high temperature electrical resistivity and thermoelectric power, magnetic susceptibility, and, eventually, the low temperature electronic specific heat. The low temperature electrical properties are not discussed here (cf. Wilson 1954; Gorter, van den Berg, and de Nobel 1956; Korringa 1956; and also the discussion following this last reference); the Hall effect is excluded because it is not yet properly analyzed in alloys, which are essentially inhomogeneous bodies; the same applies actually to the magnetic susceptibility, from which therefore only semiquantitative results may be deduced.

1. ALLOYS WITH NONTRANSITIONAL CONSTITUENTS

Their properties are fairly well understood.

1.1. Valency Effect (Norbury's Rule)

1.1.1. Resistivity

Figs. 1 and 2 recall that when impurities with increasing valencies are substituted in an 'ordinary' metal like copper or aluminum, their 'residual' resistivity $\Delta\rho$ (that is the difference between the resistivity $\rho + \Delta\rho$ of the alloy and that ρ of the pure matrix at the same temperature) increases roughly as Z^2 , if Z is the difference of valency between the two constituents: $Z = 1, 2, 3, 4$ for Zn, Ga, Ge, As respectively in copper.

This behavior can be satisfactorily explained by treating the conduction electrons of the matrix as *free* and scattered by the relatively small *perturbation* due to the impurity atoms, that is by the difference V_p between the potentials acting on the conduction electrons in the alloy and in the pure matrix.

This approximation was first justified by Tibbs (1939), as follows: To solve the Schroedinger equation

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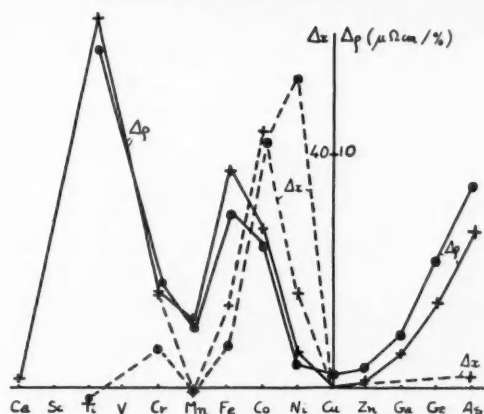


FIG. 1. Residual resistivity $\Delta\rho$ (in $\mu\Omega\text{-cm.}$ per per cent) and Δx for various substitutional impurities in copper and in gold, as a function of the difference Z of valency. Dots: gold alloys; crosses: copper alloys. Continuous lines: $\Delta\rho$; broken lines: Δx (after Linde 1931, 1932; Landolt and Börnstein 1931; Pawlek and Reichel 1956).

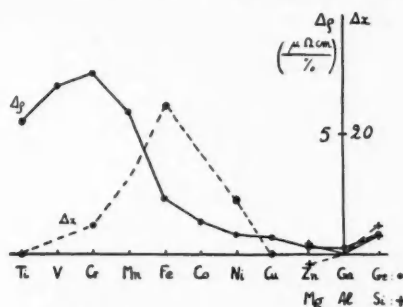


FIG. 2. Residual resistivity $\Delta\rho$ (in $\mu\Omega\text{-cm.}$ per per cent) and Δx for various substitutional impurities in aluminum. Dots: Ge, Ga, Zn, Cu ... series; crosses: Si, Al, Mg ... series. Continuous lines: $\Delta\rho$; broken lines: Δx (after Liebertz 1956; Crussard 1948).

$$(1) \quad (H + V_p)\psi = E\psi,$$

where H is the Hamiltonian of the pure matrix, we put

$$(2) \quad \psi = \psi_0\phi,$$

where ψ_0 is the wave function of the bottom E_0 of the conduction band in the pure matrix:

$$(3) \quad H\psi_0 = E_0\psi_0, \quad \text{with} \quad \int \psi_0^* \nabla \psi_0 d\tau = 0.$$

We obtain*

$$(4) \quad \psi_0 [(-\frac{1}{2}\Delta + V_p)\phi - (E - E_0)\phi] = \nabla \psi_0 \nabla \phi.$$

*Atomic units $e = \hbar = m = 1$ are used throughout this paper. To obtain $\Delta\rho$ in $\mu\Omega\text{-cm.}$, one has to multiply the value expressed in atomic units by a factor 0.24.

Tibbs' approximation is obtained by neglecting the term on the right in this equation. It should be good for most metals, especially light ones, where $\nabla\psi_0$ is very small over most of the volume (cf. Mott and Jones 1936).

We can then write, in the one-electron picture, that

$$(5) \quad \Delta\rho = \frac{1}{N_{\text{eff}}} \frac{1}{\tau} = \frac{k_M A c}{N \Omega},$$

where the effective number N_{eff} of conduction electrons is taken equal to their number N , $1/\tau$ is the impurity scattering frequency, Ω the atomic volume, k_M the momentum of the conduction electron at the Fermi limit, A the effective scattering cross section of the impurity atoms, and c their concentration. For a perturbation V_p with spherical symmetry, A may be expressed in terms of the phase shifts η_l it produces on the various spherical harmonics into which the electronic wave function may be analyzed. Thus (cf. de Faget and Friedel 1956)

$$(6) \quad \Delta\rho = \frac{4\pi c}{N\Omega k_M} \sum_l l \sin^2(\eta_{l-1} - \eta_l).$$

Fig. 3 shows that the resistivities computed in this way for copper alloys are in satisfactory agreement with experiment. The exact form assumed for

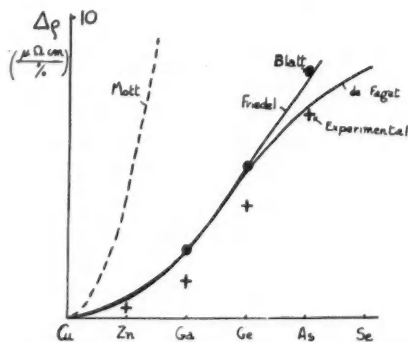


FIG. 3. Residual resistivity $\Delta\rho$ (in $\mu\Omega\text{-cm.}$ per per cent) of polyvalent impurities in copper. Crosses: experimental values (Pawlek and Reichel 1956); computed values by Mott (Mott and Jones 1936), Friedel (1954), Blatt (1955), and de Faget de Casteljaeu and Friedel (1956).

V_p does not matter very much, provided it extends over a distance from the impurity nucleus of the order of the Debye radius, that is here about r_s , the radius of the atomic sphere, and provided it displaces in the Fermi gas a screening charge just equal to the excess nuclear charge Z of the impurity. The charge displaced in the l th spherical harmonic is equal to $(2/\pi)(2l+1)\eta_l(k_M)$ (Friedel 1952); the condition is thus

$$(7) \quad 2 \sum_l (2l+1) \eta_l(k_M) = \pi Z.$$

As seen in Fig. 3, very similar results are obtained with:

(1) a screened Coulomb field (Friedel 1954)

$$(8) \quad V_p = -\frac{Z}{r} e^{-\sigma r};$$

(2) a square well (de Faget and Friedel 1956)

$$(9) \quad V_p = \text{const. for } r \leq r_s, \text{ and } = 0 \text{ for } r > r_s;$$

(3) a more self-consistent potential (Blatt 1955).

The computed values vary roughly* as Z^2 , at least up to $Z = 3$ or 4, in agreement with Norbury's rule. Mott's computation (cf. Mott and Jones 1936) also predicted such a variation, but gives too large values of $\Delta\rho$, as seen by the punctuated curve, Fig. 3. This is because the potential V_p and the phase shifts η_i are too large to be treated by a first-order perturbation method, as was done by Mott. This is easily seen from equation (7): for the localized perturbations considered, η_0 is much larger than the other η_i , and therefore of the order of at least $\frac{1}{2}\pi$ for $Z > 1$.

1.1.2. Thermoelectric Power

Using the fact that, in the one-electron picture and at temperatures not too high but higher than the Debye temperature, the thermoelectric power of a metallic substance is proportional to the logarithmic derivative of its resistivity with respect to energy at the Fermi level (Mott and Jones 1936), the relative variation in thermoelectric power with alloying may be written (Friedel 1953)

$$(10) \quad \frac{\Delta S}{S} = -\frac{1 - \Delta x/x}{1 + \rho/\Delta\rho},$$

with

$$(11) \quad x = -(E_M - E_0) \frac{d \ln \rho}{d(E_M - E_0)}$$

and†

$$(12) \quad \Delta x = -(E_M - E_0) \frac{d \ln \Delta\rho}{d(E_M - E_0)}.$$

E_M is the Fermi limit and E_0 the bottom of the conduction band.

For the fairly small perturbations V_p and the fairly large energies E_M considered here, $\Delta\rho$ should decrease slowly with increasing energy (cf. Mott and Massey 1949). Δx should therefore be *positive* and *small*, as is indeed observed for impurities in copper, silver, or gold (Fig. 4, from ΔS in Landolt

*No computation has been done for matrices other than copper; but the fact that Norbury's rule is not well followed in magnesium (Salkovitz and Schindler 1955) and aluminum (cf. Fig. 2) is not surprising a priori.

†The quantity of theoretical interest is $\Delta x/(E_M - E_0)$. The quantity Δx is preferred here because it has no dimensions. It has been computed using for $E_M - E_0$ the free electron approximation.

and Börnstein (1931) and S by various authors (cf. Otter 1956)). The figure shows that Δx is of the order of unity, in approximate agreement with the value deduced from Mott's formula for $\Delta\rho$ (cf. Friedel 1953) and from more elaborate computations (Blatt 1955; de Faget and Friedel 1956).

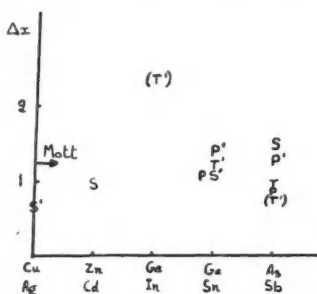


FIG. 4. Values of Δx deduced by various methods for polyvalent impurities in copper. S, S' : from thermoelectric power, equation (7); P, P' : from the variation of $\Delta\rho$ with pressure, equation (21); T, T' : from the variation of $\Delta\rho$ with temperature, equation (22). S, P, T are for Zn, Ga, Ge, As; S', P', T' for Ag, Cd, In, Sn, Sb. The arrow gives the value deduced from Mott's formula for $\Delta\rho$.

1.1.3. Magnetic Susceptibility

The Pauli paramagnetism and the Landau diamagnetism of a metal are both affected by the introduction of impurities. One usually observes a slight *increase in diamagnetism* in copper base alloys which we have attributed to the increase in the density of fairly loosely bound valency electrons kept in its neighborhood by a polyvalent impurity (Friedel 1952, 1954). But as no satisfactory theoretical analysis of either the dia- or para-magnetism exists so far for alloys, no definite conclusion may be drawn as yet (cf. recent measurements by Vogt and Friedewold (1956) and Henry and Rogers (1956)).

1.2. Period Effect (Norbury's Rule, Continued)

1.2.1. Mott's Approximation

When the atomic number of a (substitutional) impurity is increased, its residual resistivity does not increase indefinitely, but shows a periodical variation, so that the residual resistivity $\Delta\rho$ of an impurity depends mainly on its valency and little on the row it belongs to in the periodic table. In particular, the resistivity $\Delta\rho$ is very small when the two constituents of an alloy have the same valency. Figs. 1 and 2 recall these facts for alloys in copper, gold, and aluminum.

Tibbs' approximation cannot hold for such alloys, because the perturbation V_p is so large that the corrective term $\nabla\psi_0\nabla\phi$ can no longer be neglected in equation (4). We can use a method due to Mott (cf. Mott and Jones 1936) to explain the periodicity of $\Delta\rho$ in the periodic table. To separate the 'valency' and the 'period' in an alloy* $A B$, we consider the element C which has the

* $A B$ means B dissolved in A .

same period as B, but the same valency as A: for **Au Zn**, this would be copper. Let ψ_0' be the wave function of the bottom E_0' of the conduction band in the pure element C:

$$(13) \quad H'\psi_0' = E_0'\psi_0', \quad \text{with } \int \psi_0'^* \nabla \psi_0' d\tau = 0,$$

if H' is the corresponding Hamiltonian. In usual metals, ψ_0 and ψ_0' are constant near limits of the atomic polyhedra, and have similar values (the same value if we neglect the difference in size of the atomic polyhedra). If we write therefore $\psi = \psi_i \phi$ with $\psi_i = \psi_0'$ in the atomic sphere of the impurity ($r \leq r_s$) and $\psi_i = \psi_0$ outside ($r \geq r_s$), the function ϕ will be fairly continuous across the limit $r = r_s$ and satisfy the equation

$$(14) \quad \psi_0 [(-\frac{1}{2}\Delta + V)\phi - (E - E_0)\phi] = \nabla \psi_i \nabla \phi + (\psi_0 - \psi_i) [(-\frac{1}{2}\Delta + V) - (E - E_0)]\phi,$$

with

$$(15) \quad \begin{aligned} V &= V_p - (H' - H) + E_0' - E_0 & \text{for } r \leq r_s, \\ V &= V_p & \text{for } r \geq r_s. \end{aligned}$$

As for equation (4), the corrective term $\nabla \psi_i \nabla \phi$ may usually be neglected. The corrective term in $\psi_0 - \psi_i$ is different from zero only near the nucleus of the impurity, where ψ_0 and $\psi_i = \psi_0'$ have not the same number of nodes. If this term is also neglected, the conduction electrons can still be treated as *free*, but scattered by a potential V much smaller than V_p , because the large part $H' - H$ due to the difference in period has been replaced by a square potential well with a depth $E_0' - E_0$ which is usually small: the large local change $H' - H$ in potential energy is compensated by a large change in kinetic energy, leading to the replacement of ψ_0 by ψ_0' , with a different number of nodes.

1.2.2. Components with the Same Valency

The potential V is the sum of the square well, due to the difference of period, and of a term V_s due to the rearrangement of the conduction electrons in the presence of the impurity atoms. For impurities with the *same* valency as the matrix, this rearrangement is just due to the fact that the conduction electrons are slightly attracted or repelled by the impurity, depending on whether $E_0' - E_0$ is negative or positive. $E_0' - E_0$, and thus V , is usually small, and $\Delta\rho$ should be *very small*, in agreement with Norbury's rules.

With first-order approximation, a self-consistent solution is obtained by noting that Poisson's equation and a Thomas-Fermi method give (cf. Friedel 1954)

$$(16) \quad \Delta V_s = q^2 V_s$$

with

$$(17) \quad q^2 = 4\pi n(E_M),$$

where $n(E_M)$ is the density of states at the Fermi level. The required boundary conditions give, using the fact that $qr_s \gg 1$ in usual metals,

$$(18) \quad \begin{aligned} V &= V_s + E_0' - E_0 \simeq \frac{r_s}{r} \frac{\sinh qr}{\exp(qr_s)} (E_0' - E_0) & \text{for } r \leq r_s, \\ V &= V_s = -r_s [\exp q(r_s - r)] (E_0' - E_0) & \text{for } r \geq r_s. \end{aligned}$$

The rearrangement of conduction electrons thus fills the potential well to half its value at the boundary $r = r_s$ of the impurity atom, and almost completely at its center. It also produces some localized perturbation in the surrounding matrix (Fig. 5, cf. Huang 1948).

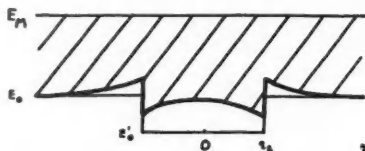


FIG. 5. Variation of potential V with distance r to the nucleus of an impurity atom, according to equation (18).

Using the fact that, for small perturbation V ,

$$(19) \quad \sin \eta_l \simeq \eta_l \simeq -\pi \int_0^\infty V J_{l+1/2}^2(kr) r dr,$$

where J_n is a Bessel function (Mott and Massey 1949), one deduces from (6) that only η_0 contributes significantly to $\Delta\rho$; thus, by a simple integration,

$$(20) \quad \Delta\rho \simeq \frac{\pi^3 c}{N\Omega k_M} (E_0' - E_0)^2 \frac{q^2 r_s^6}{\exp(2qr_s)} \left(1 + \frac{q^2 - 2k_M^2}{6} r_s^2 + \dots \right).$$

This formula leads to very small resistivities for any reasonable value of $E_0' - E_0$. More precisely, it is smaller by a factor $[q^2 r_s^6 / \exp(2qr_s)] \times [1 + \frac{1}{6}(q^2 - 2k_M^2)r_s^2 + \dots]$ than the resistivity computed by Mott for a square well potential of depth $E_0' - E_0$ (cf. Mott and Jones 1936). This factor is of the order of a few per cent for usual metals. As Mott's formula explained reasonably well the small resistivities observed in alloys like Cu Ag, Cu Au, Ag Au, we see that the more exact formula (20) gives values of $\Delta\rho$ much too small to explain the observed values; the scattering is probably due not to the perturbation V but to terms which have been neglected: the *corrective term* $\nabla\psi_i \nabla\phi$ in (14), and the lattice distortions due to the *size effect*. As comparable resistivities are observed in Ag Au with practically no size effect, and in Cu Ag, Cu Au, with a relative difference of atomic radii of the order of 15%, the corrective term $\nabla\psi_i \nabla\phi$ is probably predominant. This justifies in some degree our neglect in this paper of the size effect (cf. Klemens (1956) for a discussion of this factor).

1.2.3. Components with Different Valencies

V_s is then due to the rearrangement of conduction electrons under the action of two perturbations: (1) the square well potential of depth $E_0' - E_0$, and (2) the excess nuclear charge Z of the impurity corresponding to the difference of valency. It is easily checked that, for reasonable values of the potential well, the self-consistent perturbation due to it is negligible compared with that due to the difference of valency. The resistivity $\Delta\rho$ should then be *independent of any period effect*, in agreement with Norbury's rule. The small dependence on period observed in Figs. 1 and 2 could be due to the corrective

terms neglected in (14). The size effect should be negligible, as above, because it should lead to a correction increasing with the difference of atomic radii, thus with $|Z|$, while the variation observed is practically independent of Z .

1.3. Effect of Temperature and Pressure

The small variations of $\Delta\rho$ with these two factors lead to values of Δx consistent with those deduced from the thermoelectric power.

1.3.1. Effect of Pressure (Linde's Rule)

The application of a pressure p lowers the residual resistivity $\Delta\rho$ of polyvalent impurities in copper, silver, and gold. This can be explained by the increase of Fermi energy $E_M - E_0$ due to the reduction of the volume V of the alloy. Treating the conduction electrons as free, $E_M - E_0$ is proportional to $V^{-2/3}$; thus, from (12), (Linde 1949)

$$(21) \quad \frac{d\Delta\rho}{\Delta\rho dp} = \frac{d \ln \Delta\rho}{d \ln(E_M - E_0)} \frac{d \ln(E_M - E_0)}{d \ln V} \frac{d \ln V}{dp} = -\frac{2}{3}\chi\Delta x,$$

if χ is the compressibility of the metal. Fig. 4 shows that values of Δx thus deduced from the observed values of $d\Delta\rho/dp$ (from Linde 1949) are in good agreement with those deduced from the thermoelectric power.

1.3.2. Effect of Temperature (Deviations from Matthiessen's Rule)

According to the well-known Matthiessen rule, the residual resistivity Δx does not vary with temperature. This expresses the fact that the scattering by impurities and by thermal agitation is incoherent (cf. Mott and Jones 1936).

Small deviations from this rule are observed in the 'normal' alloys discussed in this section, corresponding to an increase of $\Delta\rho$ with temperature (Linde 1931, 1932, 1949). There are two reasons for this deviation: the thermal expansion $\alpha = dV/VdT$, leading to a shift in the Fermi level, and a term analogous to (21); and a variation of the elastic constants of the alloy with composition, which alters the scattering due to thermal agitation. As the thermal scattering is proportional to T and to an elastic constant such as the compressibility χ (at least above the Debye temperature), the following equation should hold for small concentrations c :

$$(22) \quad \frac{d\Delta\rho}{\Delta\rho dT} = \frac{2}{3}\alpha\Delta x + \frac{cd\chi}{\chi dc} \frac{d\rho}{\Delta\rho dT},$$

where ρ is the resistivity of the pure matrix.*

Polyvalent impurities increase the compressibilities of copper, silver, and gold by amounts roughly proportional to the difference Z of valency with the matrix. The second term in $d\Delta\rho/\Delta\rho dT$ thus varies roughly as $1/Z$, while the first one is roughly a constant. Such a behavior is indeed observed (Linde *loc. cit.*),† and Fig. 4 shows that reasonable values of Δx are deduced from

*The corrective term in (21) analogous to the second term in (22) would involve the variation of Grüneisen's constant (or of $d\chi/\chi d\rho$) with composition in an alloy; it is therefore not well known, but likely to be small.

†Norbury and Kuwada's law (1927) that $d\Delta\rho/dT$ is a linear function of $\Delta\rho$, thus of Z^2 , is not well followed (Hansen, Johnson, and Parks 1951), no doubt because $cd\chi/\chi dc$ varies with Z .

experiment, after correction for the second term in (22) from measurements of elastic constants in alloys by Köster (1948) and Smith (1952). Values of Δx obtained for alloys with small Z 's, like **Cu** In, are of course only approximate.

A small effect of a similar kind should hold for the *residual thermoelectric power* ΔS . In metals like copper, it may however be masked by the variation of x itself with temperature (Domenicali and others 1954, 1955; Blatt 1955). According to equation (10), a variation of x will affect ΔS most strongly when they are both of the same sign and of the same order of magnitude. In copper, silver, and gold, x is of the order of -1 to -2 (Mott and Jones). Negative values of Δx of that order are not observed with 'ordinary' impurities; but they are characteristic of some *transitional* impurities to which the same analysis applies (cf. §2). Fig. 6 shows, for instance, that, in **Cu** Mn alloys,

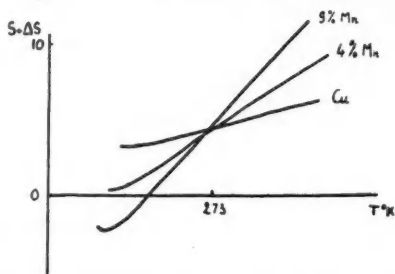


FIG. 6. Thermoelectric power $S + \Delta S$ (in $\mu\text{V}/^\circ\text{C}$.) of **Cu** Mn alloys, against temperature T (in $^\circ\text{K}$.), for various concentrations of manganese (Otter 1956).

ΔS changes its sign around 0°C ., in agreement with the fact that, in copper, x increases with temperature and goes at 0°C . through a value -1.9 equal to that of Δx of Mn as deduced from high temperature measurements of ΔS (Otter 1956).

1.4. Effect of Concentration (Nordheim's Rule)

It is usually observed that in disordered solid solutions the *resistivity* $\Delta\rho$ varies in a parabolic way with the concentration c :

$$(23) \quad \Delta\rho = ac(1-c) + bc.$$

a and b are two constants. As usually $a \gg b$, $\Delta\rho$ is almost proportional to c up to fairly large concentrations ($c \leq 0.20$).

This rule has been explained by Nordheim (1931) and others (Mott and Jones 1936; Muto 1938) using *first-order* approximation methods to compute both the effective number N_{eff} of conductive electrons and their frequency of scattering $1/\tau$ in equation (5).

Such an approximation may be valid for N_{eff} , although corrections should be introduced for alloys with components of different valencies (Z large, cf. Friedel 1954). But it is unsatisfactory as regards $1/\tau$ for two reasons: (1) except for components with the same valency ($Z = 0$), it cannot be used to compute

the effective scattering cross section A (cf. §1.1.1); (2) it also assumes for the electrons a Fermi velocity constant over the whole volume of alloy, thus varying with its composition; electrons arriving on an impurity atom will on the contrary have a Fermi velocity equal to that in the pure matrix, as long as the perturbations due to the various impurity atoms do not interact, that is up to fairly high concentrations because these perturbations are highly localized in ordinary alloys* (cf. Friedel 1952, 1954).

Deviations from Nordheim's parabolic rule should therefore not be surprising, especially with components of very different valencies. It would probably be hard to develop an approximation better than Nordheim's (cf. Parmenter 1955). This would however be essential to study the effect of short-range order on resistivity in alloys like **Cu Zn** with $Z \neq 0$ (cf. Gibson 1956). The effect of order will therefore not be discussed here.

As shown in Fig. 7 for Ag Au solid solutions, the *thermoelectric power* of a disordered alloy usually exhibits a strong positive curvature towards the concen-

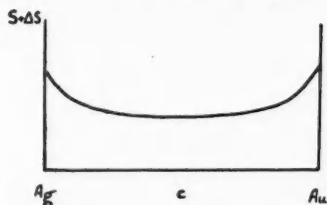


FIG. 7. Thermoelectric power $S + \Delta S$ of Ag Au solid solutions against atomic concentration c , exhibiting strong curvatures at the two ends of the diagram (Table des constantes 1913).

tration axis with increasing concentration of impurity. This characteristic behavior comes from the fact that, in equation (10), the residual resistivity $\Delta\rho$ becomes larger than the resistivity ρ of the matrix for relatively small concentrations. The measured values of ΔS usually lead to values of Δx which are fairly *independent* of concentration, up to fairly large concentrations, at least for impurities in copper, silver, or gold (Friedel 1953). This confirms the picture of impurity centers scattering independently of each other up to these concentrations. With a constant Δx , the thermoelectric power should have a horizontal asymptote,

$$(24) \quad S + \Delta S \rightarrow \frac{\Delta x}{x} S = \frac{\pi^2}{3} \frac{\Delta x}{E_M - E_0} k^2 T,$$

which should be practically reached when impurity scattering predominates over that due to thermal agitation ($\Delta\rho \gg \rho$), or for $c > 0.05$ to 0.20 for usual alloys at room temperature. This horizontal plateau is indeed observed in most alloys with Cu, Ag, or Au; and it varies *linearly with temperature*, in agreement with (24), up to values of T where scattering by thermal agitation becomes important (cf. Domenicali and Otter 1955). The same behavior is observed for transitional impurities, as shown in Fig. 6 for **Cu Mn** (Otter 1956).

*The fact that the Fermi energy E_M does not depend on concentration at infinite dilution has been used to obtain equation (10).

1.5. Deviations from the Free Electron Approximation

Two approximations have been made in computing N_{eff} and $1/\tau$ in equation (5):

- (a) correlations between conduction electrons have been neglected,
- (b) conduction electrons have been assumed free.

Optical measurements seem to indicate in usual metals values of N_{eff} not very different from the free electron ones N ; in copper, N_{eff} is apparently somewhat smaller than N ; the corresponding correction on $\Delta\rho$ is in the right direction to explain the small discrepancies of Fig. 1.

The corrections on $1/\tau$ have not, on the other hand, been worked out so far down to numerical values (cf. Köster 1954; Pines 1955). They are likely to be small:

(a) as $1/\tau$ does not depend very much on the exact form of the perturbation (cf. §1.1), it is probably not much affected by the small corrections due to correlation.

(b) *the conduction electrons must behave more like free electrons in the neighborhood of an impurity than in the matrix.**

This conclusion may be reached by noting that the fairly localized perturbation V_p of an impurity atom must mix up Bloch states from neighboring energy bands (Adams 1953), or that conduction electrons receive a fairly strong and sudden impulse when arriving in the neighborhood of such an atom (Mott 1955).

The condition for the effective mass corrections to be negligible for $1/\tau$ must be something like†

$$(25) \quad |\nabla V_p|/(E_M - E_0) \geq k_M$$

in the region $r \leq a$ where V_p is not negligible and thus where it is at least of the order of $E_M - E_0$.

Replacing $|\nabla V_p|/(E_M - E_0)$ by $1/a$, we see that condition (25) is approximately fulfilled in the alloys considered here, because the radius of screening a is of the order of $1/k_M$ in ordinary metals.‡ This explains why the free

*The same tendency towards free electron behavior occurs of course by melting, in metals like Ga, Sb, Bi (cf. Mott and Jones 1936), and somewhat above the melting point in the divalent metals Mg, Zn, Cd, Hg (Scala and Robertson 1953).

†This almost self-evident condition can be seen from equation (4) or (14). The deviations from free electron behavior are due to the corrective term $\nabla\psi_0\nabla\phi$. In a perfect lattice, where $\phi = \text{const. exp}(i\mathbf{k}\cdot\mathbf{r})$ in first approximation, this introduces a corrective potential $i\mathbf{k}\nabla\psi_0/\psi_0$ with the periodicity of the lattice and an average value $i\mathbf{k}\int\psi_0^*\nabla\psi_0 d\tau = 0$ (because ψ_0 has an average velocity equal to zero). This correction therefore alters ϕ by a resonance mechanism. A perturbation V_p which varies rapidly enough with distance will increase the variations of $\nabla\phi$ in space, but destroy its coherency with $\nabla\psi_0$ in the region of scattering where $V_p \neq 0$. The resonance effect is certainly destroyed when the contribution to $\nabla\phi$ from the variation of V_p in space exceeds the value of $\nabla\phi$ in the periodic lattice. According to equation (4), the two contributions are respectively $|\nabla V_p/(E - E_0)|\phi$ and $i\mathbf{k}\phi$; condition (25) is thus obtained. Except for very special perturbations V_p , $\nabla\phi$ and $\nabla\psi_0$ are then likely to be completely incoherent over the scattering region; the corrective term should thus have a small average value: $\int\psi_0^*\phi^*\nabla\psi_0\phi d\tau \approx \int\psi_0^*\nabla\psi_0 d\tau \int\phi^*\nabla\phi d\tau \approx 0$, and therefore be negligible in that region.

‡Condition (25) is not fulfilled for the perturbations V_p due to thermal agitation; the effective mass approximation is certainly valid in that case (cf. Radcliffe 1955; Barrie 1956).

electron approximation gives reasonable values of $\Delta\rho$ and Δx in metals like copper where the Fermi surface is known, from thermoelectric power and other measurements, to deviate markedly from a sphere (Mott and Jones 1936).

1.6. Impurities in Polyvalent Metals

There seems to be some evidence that the residual resistivity $\Delta\rho$ and thermoelectric power ΔS of an alloy vary with the filling of its various energy bands. This is observed for instance for impurities in polyvalent metals, where two bands overlap in the neighborhood of the Fermi level. Thus in magnesium the variations with concentration of $\Delta\rho$ and $d\Delta\rho/dT$ change their slopes, and ΔS changes its sign for the critical electron per atom ratio 2015 where a new energy band begins to be filled (Schindler and Salkovitz 1955; Salkovitz and Schindler 1955; Kammer, Salkovitz, and Schindler 1955). The fairly large ΔS (and Δx) observed in aluminum alloys (Fig. 2) has also been tentatively explained as due to a change in the filling of the small empty 'pockets' left in the first Brillouin zone occupied by the conduction electrons in aluminum (Galt 1949; Friedel 1953).

This dependence on the band structure is not easy to analyze, because it may have two different origins:

(a) Impurity scattering: As pointed out above, the residual resistivity varies with the effective number N_{eff} , which will vary with the degree of filling of the bands. For concentrations large enough for the impurities to interact, the frequency of scattering $1/\tau$ will also be altered by a change of filling of the bands.

(b) Change in thermal scattering, due to the change in electronic structure with the filling of the bands.*

These two effects have not yet been properly estimated. The usual treatment by first-order approximation assumes the alloy to have the same energy band structure as the pure matrix. Alloying will certainly tend to blur out the details of this structure (cf. Friedel 1954). The effects due to Brillouin zone boundaries will therefore be less marked than predicted by this approximation.

2. ALLOYS WITH TRANSITIONAL SOLUTE ELEMENTS

Figs. 1 and 2 show that, in copper and in aluminum, $\Delta\rho$ and Δx vary in a somewhat irregular way with the atomic number of the solute element, when this is a transitional element (Ni, Co, Fe, Mn, etc.). The strong *peaks* observed suggest some resonance process between the conduction electrons and the *d* shells of the solute elements, which become progressively empty when one goes through the series of these elements. As first pointed out by Linde (1949) and considered in more detail by de Faget de Casteljau and Friedel (1956), an analogous resonance effect may be observed in the scattering of free electrons by free atoms. This effect will be first recalled, then compared with what is observed in aluminum alloys and copper alloys.

2.1. Resonance Scattering of a Beam of Free Electrons by the Atoms of a Gas

This is observed when the potential V provided by the atoms is not quite strong enough to accept a certain bound state: if the atomic potential $V(r)$

*This effect has been neglected in equation (22).

of Fig. 8 was along the punctuated curve, it would accept, say, a bound state $3d$ below the bottom of the continuum of free electrons. As V becomes less attractive, the energy of this bound state increases; we suppose that it has merged

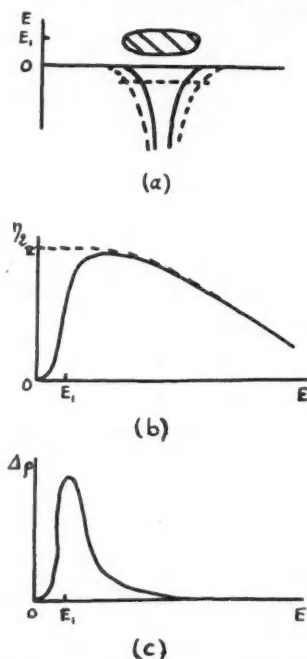


FIG. 8. Virtual $3d$ bound state for a potential $V(r)$ with spherical symmetry. (a) Representation of the state in energy and space. (b) Variation of the corresponding phase shift η_2 with energy. (c) Variation with energy of the resistivity $\Delta\rho$ (or of the scattering power). Continuous curves: virtual bound state; broken curves: real bound state, for a slightly more attractive potential V .

into the continuum of states with positive energies when V has reached the position of the continuous curve. The $3d$ bound state has then disappeared. For sake of convenience, we may say that it has now a (small) positive energy E_1 ; but it resonates with the free electron state with the same energy, to give two states with slightly different energies; these states will also resonate with states of the continuum, and so on. The $3d$ bound state is thus no longer well defined in the energies nor in space. Its existence is marked only by an increase in amplitude, near the origin and for a narrow band of energy w , of the d spherical component of the wave functions of the scattered electrons (Fig. 8a). The resonance process has not altered the fact that the perturbation has introduced five more states with two spin directions in the neighborhood of energy E_1 . Using formula (7), we can conclude that the phase shift η_2 must increase rapidly from small values to values near π in the band of energy w centered on energy E_1 (Fig. 8b). The other phase shifts vary usually slowly

in that range, and those with $l > 2$ are usually small. According to (6), we expect thus a strong maximum of scattering when $\eta_2 \simeq \frac{1}{2}\pi + \eta_3 \simeq \frac{1}{2}\pi$, thus for an energy near E_1 (Fig. 8c). One may say that the resonance process which broadens the $3d$ state with positive energy also increases the scattering of the free electrons. Some peaks observed in the scattering of slow electrons by free atoms are explained in this way (cf. Mott and Massey 1949).

Some properties of the broadened or 'virtual' bound states with positive energy are of interest:

(1) Their broadening w increases with their average energy E_1 .

(2) For a given energy E_1 , the broadening decreases with increasing values of quantum number l ($l = 0, 1, 2 \dots$ for s, p, d, \dots harmonics). For s harmonics, the broadening is actually so large that the corresponding virtual states lose their physical meaning ($w \gg E_1$, cf. Schiff 1955).

These results follow directly from the fact that the broadening w of a virtual bound state of l symmetry and energy E_1 is essentially proportional to the amount of l th harmonic in the electronic wave function with energy E_1 (cf. §2.4).

2.2. Aluminum Alloys

We consider now the series of alloys of Fig. 2. A solute atom like copper or zinc has certainly a d shell stable enough to be completely full: all its d electrons have energies below the Fermi level of aluminum. A solute atom like calcium or titanium, on the other hand, has probably a nearly empty d shell: the d electrons have all energies above the Fermi distribution. In the series of transitional elements from the former to the latter, the d electrons are continuously shifted towards higher energies; they must therefore go through the Fermi level E_M of aluminum at some point. d states with energies near E_M must resonate with the conduction electron states in the conduction band of aluminum, and lead to broadened virtual d states analogous to those discussed above.

We expect therefore a peak in the resistivity $\Delta\rho$ when such a d state crosses the Fermi level. Fig. 2 shows that *one broad peak* of resistivity is effectively observed around chromium. The fact that $\Delta\rho$ varies fairly continuously with the atomic number of the impurity, and shows only one peak, seems to indicate that in this case the d shells of the transitional elements form *one broad virtual 3d state, with room for $2 \times 5 = 10$ electrons*, which empties itself continuously when one goes from copper to titanium (Fig. 9a, cf. de Faget and Friedel 1956). This conclusion is confirmed by the behavior of Δx : from equation (12), one expects Δx to vary roughly as the derivative of $\Delta\rho$ with the atomic number of the impurity; more precisely, one expects a strong peak of positive values when the d shell begins to empty itself (Co, Fe), and then a smaller peak of negative values for nearly empty and broader d shells of higher energy (E_1 (Ti, etc.)). Fig. 2 shows that this is roughly what is observed.

The fact that there is only one peak, thus one broad $3d$ virtual state, is important. It shows that the resonance broadening we have discussed is large compared with the factors which could split the state. These are:

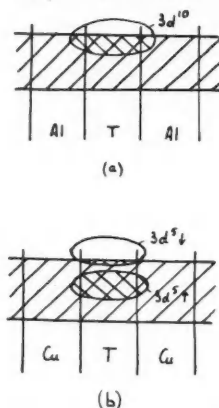


FIG. 9. Virtual $3d$ bound states of a transitional element T : (a) in aluminum; (b) in copper. E_M is the Fermi limit.

- (1) the cubic symmetry of the lattice, which tends to split d states of the x^2-y^2 and of the yz types;
- (2) the coulomb correlation interactions, which tend to separate the various degrees of ionization of the $3d$ shells ($3d^{10}$, $3d^9$, $3d^8$, etc.);
- (3) the exchange interactions, which could tend to stabilize the electrons with one spin direction with respect to those with the other.

As a consequence, the band or 'molecular' approximation seems to be applicable in this case; one can treat *all* the electrons in the same average field of potential, whatever their spin direction, and whether they come from the conduction band of the matrix or from the d shell of the impurity.

In agreement with this conclusion, the transitional elements dissolved in aluminum exhibit a simple *increase in para- or dia-magnetism, fairly independent of temperature*, which can be attributed (1) to a variation of Pauli paramagnetism, due to the increase in the density of states when a virtual d state overlaps the Fermi level; or (2) to an increase in Landau diamagnetism, due to a nearly

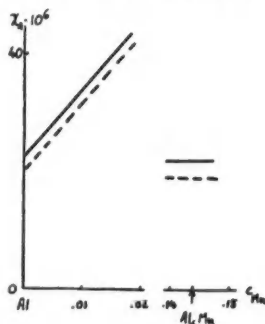


FIG. 10. Molar susceptibility of Al-Mn and Al_6Mn against atomic concentration of manganese. Continuous curves: 82°K ; broken curves: 293°K . (after Vogt 1954).

full and broadened d shell. Fig. 10 shows for instance the fairly strong increase in paramagnetism observed for Al Mn and for the intermetallic compound Al₆ Mn (Vogt 1954). Measurements at 83° and 293° K. show that it is fairly independent of temperature (cf. also Foëx and Wucher 1954, 1956).

2.3. Copper (and Silver, Gold) Alloys

2.3.1. Electrical Properties

Fig. 1 shows that in this case *two* peaks of resistivity $\Delta\rho$ are observed, with about equal strength and width. This seems to indicate that the d shell of an impurity gives rise to *two* $3d$ states with different energies, which become empty successively (Fig. 9b). Two other observations agree with this picture:

(1) The values of Δx deduced from the *thermoelectric power* vary roughly as the derivative of $\Delta\rho$ versus the atomic number of the solute element, as in aluminum alloys.

(2) There should be, in the variation of $\Delta\rho$ with temperature, a correction to equation (22) due to the curvature of $\Delta\rho(E)$ at the Fermi limit. Using a formula developed in Mott and Jones (1936), this is

$$(26) \quad \left(\frac{d\Delta\rho}{\Delta\rho dT} \right)' = \frac{\pi^2}{3} k^2 T \left[\frac{d^2\Delta\rho}{\Delta\rho dE_M^2} - 2 \left(\frac{d\Delta\rho}{\Delta\rho dE_M} \right)^2 - \frac{d\Delta\rho}{\Delta\rho dE_M} \frac{dn}{ndE_M} \right],$$

where k is the Boltzmann constant, and n the density of states at the Fermi limit. For nearly free electrons in the matrix, $dn/ndE_M \simeq 1/2(E_M - E_0)$. For fairly narrow d states such as those in Fig. 1, the term in $d^2\Delta\rho/\Delta\rho dE_M^2$ should be predominant. It expresses the fact that, for increasing temperature T , the average of $\Delta\rho$ over the Fermi distribution increases or decreases, depending on the curvature of $\Delta\rho$. The succession of two peaks of $\Delta\rho$ should correspond to a curvature in $\Delta\rho$, thus to a term $(d\Delta\rho/\Delta\rho dT)$, alternating rapidly in sign with varying atomic number. Such an oscillating behavior of the departure from Matthiessen's rule is indeed observed in these alloys at room temperature. It is superimposed on a general trend towards in-

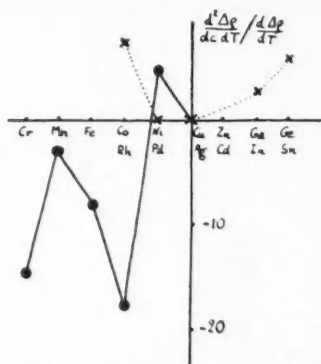


FIG. 11. Relative deviation $\frac{d^2\Delta\rho/dTdc}{d\Delta\rho/dT}$ from Matthiessen's rule, for gold alloys at room temperature (from Linde 1931). Continuous line: Ni, Co... series; broken line: Cd, Ag, Pd... series.

creasingly negative values of $d\Delta\rho/dT$, which may be due, according to equation (22), to the fact that such transitional impurity increases the stiffness of the matrix (Fig. 11). Fig. 12 shows that these deviations from Matthiessen's

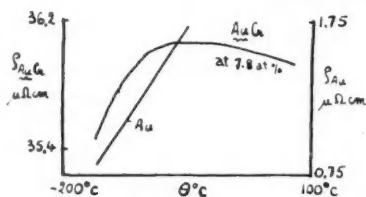


FIG. 12. Variation of resistivity with temperature in gold and in a Au-Cr alloy (Linde 1931).

rule are small for low temperature T , and increase in a parabolic way with T , as expected for the corrective term (26). This is of course the usual behavior in alloys of this kind, such as constantan.

2.3.2. Magnetic Properties

It is well known that Fe, Mn, Cr, etc. dissolved in copper, silver, and gold are strongly paramagnetic. Their susceptibility may be written as:

$$(27) \quad \chi = \frac{C}{T} + \chi_{\infty},$$

where the Curie constant C is usually large and the constant term χ_{∞} fairly small. In other words, if χ is written as equal to $C/(T - \theta)$, the Curie temperature θ is usually small, at least at small concentrations. Fig. 13 gives as an example the susceptibility χ of Cu-Mn alloys of various concentrations versus $1/T$ (after Myers 1956). In such an alloy, the effective

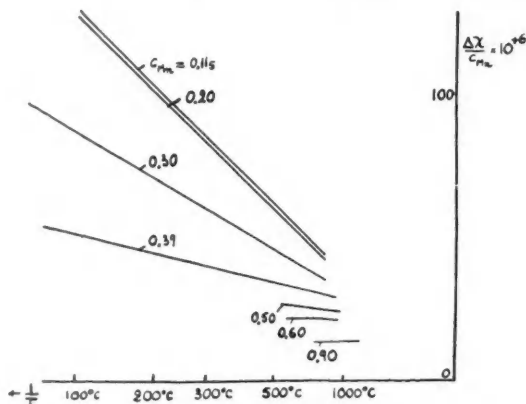


FIG. 13. Paramagnetic susceptibility χ of Cu-Mn alloys of various concentrations (per mole of manganese), against $1/T$ (after Myers 1956).

Bohr magneton number per solute atom is fairly independent of concentration up to a large concentration (Fig. 14); it corresponds nearly to the value 5 expected for a $3d^5$ shell with the five spins parallel.

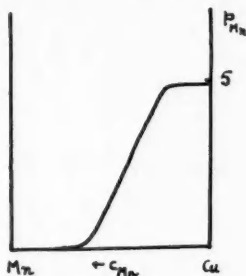


FIG. 14. Effective Bohr magneton number per Mn atom in Cu-Mn alloys (Myers 1956).

These observations seem to indicate that in such alloys, the d shell of the impurity splits into *two halves* $3d^5$ with *opposite spin directions* and different energies, which empty themselves successively (Fig. 3b). Manganese, corresponding to the minimum of $\Delta\rho$ between the two peaks, would have a $3d^5$ shell with one spin direction nearly empty and the other $3d^5$ shell nearly full, thus an effective magneton number near 5, in agreement with experiment.

2.4. Broadening of Virtual Levels

The question whether a $3d$ level will split into two states of different spin directions or not could be settled a priori if one knew the broadening w of these levels. As in a free atom, the d electrons or d holes* of the solute element will gain some exchange energy by making their spins parallel. If the d level is broad, this spin alignment requires the expenditure of some kinetic energy. The splitting will therefore only occur if the gain in exchange energy is large compared with the width w of the d level. An approximate condition for splitting will be

$$(28) \quad p\Delta E \gg w,$$

where p is the number of d electrons or d holes of the impurity and ΔE the difference of energy of a pair of d electrons or holes with spins parallel or antiparallel. The analysis of atomic spectra, and of the analogous problem of para- or ferro-magnetism of the pure transitional metals, leads to values of ΔE between 0.5 and 1 ev. for all transitional elements (cf. Friedel 1957). As $p \leq 5$, one expects a splitting of the two spin directions, two peaks in the resistivity curve, and a magnetic susceptibility following a Curie law only if the width w of the d state is much less than about 5 ev. when the state reaches the Fermi level.

Now, as we shall see, w is of the order of that critical value in ordinary metals, and increases with the kinetic energy $E_M - E_0$ of the Fermi gas of the

*More exactly the part in the wave functions of the conduction electrons of the alloy that comes from the d shell of the transitional impurity.

metal. One expects therefore a splitting of the spins only in metals with a relatively small value of $E_M - E_0$, like copper, silver, and gold, not in metals with large $E_M - E_0$ like aluminum and polyvalent metals in general; even in Cu, Ag, and Au, the splitting is only expected for impurities like Fe, Mn, Cr, V with large enough values of p , that is with d shells which are not too empty or too full. The magnetic susceptibility χ of Cu, Ag, or Au with small concentrations of Ni, Pd, Pt, and Co seems indeed to vary little with temperature T , indicating that, as in aluminum alloys, there is no (or very little) splitting of the spin directions in that case (cf. Fig. 15 for **Au** Ni, according

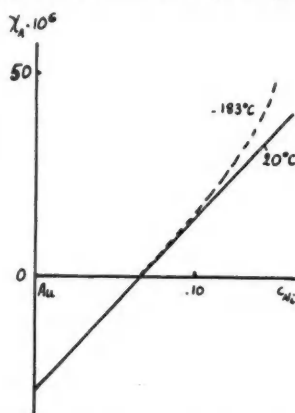


FIG. 15. Paramagnetic susceptibility of **Au** Ni. Continuous curve: $-183^{\circ}\text{C}.$; broken curve: $20^{\circ}\text{C}.$ (Vogt and Krüger 1933).

to Vogt and Krüger (1933); cf. also Weil (1941), Vogt (1951), Kaufman and Starr (1943), Hildebrandt (1937), etc.). The paramagnetism of the Pauli type usually observed in these cases may be due, as in aluminum alloys, to an increase in the density of states due to the presence of the virtual d level; it is actually of the same order of magnitude as the increase of *low temperature specific heat* also observed in **Cu** Ni for instance (Keesom and Kurrelmeyer 1940). The fact that Pd does *not* change appreciably the diamagnetism of Cu, Ag, or Au (Borelius 1934) is probably due to the fact that in this case the increase in Pauli paramagnetism is small, because the d shell of Pd is especially stable, being so far below the Fermi level of the matrix.

We have finally to prove that the width w of a virtual d state increases with the difference $E_1 - E_0$ of energy between its average energy E_1 and the energy of the bottom of the band E_0 .

As the electronic wave functions ψ of the alloy are obtained by a resonance effect between Bloch functions ψ_B and a bound level $\psi_1(E_1)$, we write

$$\psi(E) = \psi_B(E) + \sum_n a_n \psi_n(E_n),$$

with

$$H\psi_B = E\psi_B,$$

$$(H + V_p)\psi_n = E_n\psi_n.$$

H is here the Hamiltonian of the unperturbed lattice, and V_p the perturbation due to the impurity. The bound states ψ_n obey definite boundary conditions: they are assumed to vanish outside the atomic sphere S of the impurity. They form therefore a complete orthonormal set, and the development of $\psi - \psi_B$ is exact in the volume V of the sphere S . With the help of equation (1), the parameters a_n are found to be given by

$$a_n = \frac{\int_V \psi_B V_p \psi_n^* d\tau}{E - E_n} - \frac{\int_S [\psi_n^* \nabla(\psi - \psi_B) - (\psi - \psi_B) \nabla \psi_n^*] dS}{2(E - E_n)}.$$

If the energy considered, E , is near the energy E_1 of the bound level ψ_1 and far from all the others, E_n , that is if

$$|E - E_1| \ll |E_1 - E_n| \quad \text{for } n \neq 1,$$

only one parameter is important:

$$|a_1| \gg |a_n| \quad \text{for } n \neq 1.$$

Using the boundary condition for ψ_n , the surface integral is then seen to vanish to a first-order approximation:

$$a_1 \simeq (\int_V \psi_B V_p \psi_1^* d\tau) / (E - E_1).$$

In the development of ψ , the term $a_1 \psi_1$ is then negligible compared with ψ_B when

$$|E - E_1| \gg w = |\int_V \psi_B(E_1) V_p \psi_1(E_1) d\tau|.$$

In the integral, ψ_B and ψ_1 have been normalized over the volume V of the atomic sphere.

w may thus be called the width of the virtual bound state E_1 . In the case discussed in this paper, V_p has approximately a spherical symmetry and ψ_1 has d symmetry. *The width w increases with energy E_1 as the d character in the Bloch function $\psi_B = u_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}$.* For usual metals, $u_{\mathbf{k}}$ has mainly s (and a little p) character. w therefore increases mainly as the proportion of d (and also a little of p) character in the plane wave $e^{i\mathbf{k} \cdot \mathbf{r}}$ with energy E_1 . A simple computation shows that w increases therefore rapidly with E_1 , starting from zero for $E_1 = E_0$, the energy at the bottom of the band. Also, for $E_1 - E_0$ of the order of 5 to 10 ev., w is of the order of a few ev.

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DISCUSSION OF FRIEDEL'S PAPER

Dugdale: Because of the strong dependence of $\Delta\rho$ on energy would one not expect a marked pressure dependence of $\Delta\rho$? If so one would expect a change of sign in the pressure coefficient of the different alloys of aluminum in going from those on the left to those on the right of chromium (where the maximum $\Delta\rho$ occurs).

Friedel: I agree, but I have not yet calculated the magnitude of the pressure effect.

Gerritsen: Have you considered any polarization effects?

Friedel: Such effects should be especially important in an alloy like AgPd; here the d shell of the impurity is certainly less stable than that of the matrix, but it is nevertheless still strongly diamagnetic and therefore probably full. The residual resistivity is actually small in this case, and Mathiessen's rule well obeyed (Linde *loc. cit.*). This seems to indicate that polarization effects play no significant role in the electrical properties of alloys.

Seeger: If the wave function for copper calculated by Fuchs with the correct number of nodes is replaced by a function with no nodes (i.e. plane waves), the difference between the functions near the boundary of the Wigner-

Seitz cell is less than 2%. This suggests that the difference in period of the solute from the solvent should not be so important.

Friedel: In equation (14) of my paper, the term you are referring to is due to the fact that the wave functions ψ_0 and ψ_i have not quite the same value in the region where they are nearly constant, near the limit of the atomic polyhedra. But there are two other terms, important in the small region near the nuclei:

1. the corrective term in $\nabla\psi_i\nabla\phi$, because ψ_i oscillates rapidly,
2. the corrective term in $(\psi_0 - \psi_i)$, because ψ_0 and ψ_i take very different values: they don't have the same number of nodes.

These three terms are admittedly likely to be small, but not necessarily negligible when compared to the small measured resistivities.

ELECTRICAL RESISTANCE DUE TO LATTICE IMPERFECTIONS IN METALS¹

BY P. G. KLEMENS²

The electrical resistance of metals is due to the scattering of electrons by the irregularities of the crystal lattice. The thermal displacements give rise to the intrinsic resistance, while the static imperfections cause the residual resistance.

For our purpose the imperfections can be divided into two groups: point imperfections (vacancies, impurities, interstitials) and extended imperfections (dislocations, stacking faults, grain boundaries). All these scatter electrons to a varying degree, and as long as the scattering probability varies only slowly with electron energy, the resulting resistivity is independent of temperature, and can be measured fairly easily.

The electrical resistivity, particularly at low temperatures, is thus a sensitive indicator of the perfection of the crystal lattice. Unfortunately, however, this resistance is characterized by one parameter only, and gives no information about the nature of the imperfection responsible for it. In the similar case of thermal conductivity by lattice waves we are more fortunate, for different types of imperfections give rise to thermal resistivities of different temperature dependence, so that we can deduce the nature of the principal imperfections, as well as some information about their concentration. In the case of electrical resistance this is not possible, except perhaps in the case of chemical impurities. Some information can be obtained from supplementary measurements, such as stored energy, density, hardness, as well as by studying the changes on deformation or irradiation, followed by controlled annealing. In some cases useful information can also be derived from simultaneous measurements of the lattice thermal conductivity.

In view of the complexity of the experimental situation it is extremely desirable to have reliable theoretical estimates of the scattering cross-section, and thus of the electrical resistivity, of various model imperfections. In some cases, notably for point imperfections, we can have some measure of confidence in the results of such calculations, but generally only a crude order of magnitude can be given, and sometimes even that is questionable.

To calculate the electrical resistance, we must know the difference between the actual potential at the imperfection and the potential of the unperturbed lattice. The scattering of electrons can then be readily determined, provided the electron wave functions are known. Up to date it has been usually assumed that the electrons are free, so that these calculations can apply, at best, only to monovalent metals. Secondly, the potential of an ion is not always well known, and this applies, even more so, to the potential at an imperfection.

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There is usually a redistribution of the charge due to the conduction electrons; the free electrons may spend more or less time near the imperfection, and some of the conduction electrons may enter bound states about the imperfection.

There is usually some lattice distortion about an imperfection, and there is, in general, little information about such lattice distortion.

In the case of extended imperfections there is a further difficulty: the lattice sites of the unperturbed lattice are not necessarily uniquely defined.

POINT IMPERFECTIONS

In the case of point imperfections the main problem is to determine the effective scattering potential, including screening, and to take account of the effect of lattice distortion.

To calculate the resistivity of a polyvalent impurity in a monovalent metal, Mott (1936) replaced the impurity by the Coulomb field of a point charge, equal to the charge excess of the impurity ion, and screened by the conduction electrons according to the Thomas-Fermi equation. This model gave resistivities of the right order of magnitude, though somewhat too large, and explained the importance of the valence difference.

Since then there have been many attempts to refine such calculations. The electrical resistivity of dilute alloys has been discussed at this Conference by Dr. Friedel. I would like to confine myself to the resistivity of vacancies and interstitials. The development which made their estimation feasible is Friedel's (1952) sum rule.

Given a scattering potential, one can evaluate the asymptotic phase shifts η_l of the partial waves. Then the sum

$$\frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \eta_l$$

for electrons of wave number k denotes the charge localized around the scattering center, which is contributed by electrons of wave number less than k ; in particular $N(k_f)$ is the total charge screening the imperfection, which must, of course, be equal to the charge excess of the imperfection, while $N(0)$ is the number of electrons in bound states.

This provides a partial check on the self-consistency of a potential, or it enables one to adjust a parameter of a trial potential. As long as the scattering is due to partial waves of low angular momentum only, the scattering potential would not be extremely sensitive to the choice of the potential, provided the sum rule is satisfied.

Jongenburger (1953) used this method to calculate the scattering by vacancies. As scattering potential he used the negative of the Hartree potential of a copper ion—to account for the missing ion—and the potential of a hole in the uniform charge distribution of the conduction electrons, to account for screening. This potential did indeed closely satisfy the sum rule. A similar result was obtained by using a square-well potential, adjusted to satisfy the sum rule.

Blatt (1955) has similarly calculated the resistance due to interstitials, as well as due to Ga, Ge, and As in copper. In the case of the impurities, the calculated resistance is twice the observed resistance.

In these calculations the effect of lattice distortions has been neglected. This is probably justified in the case of vacancies, where the distortion is small. Jongenburger calculated that the nearest neighbors are displaced by only 1.5% of the interatomic distance. But in the case of interstitials, the distortion is much larger. According to Huntington (1952), the nearest neighbors are displaced by about 20%.

On the assumption that electrical resistance is proportional to the mean square displacement of the atoms, knowing the resistance corresponding to the mean square thermal displacement at room temperature, Jongenburger (1955) estimated the resistance due to the lattice distortions around an interstitial. This, of course, neglects any correlation effects between the displacement of neighboring ions, and any possible systematic interference. It turned out that the resistance due to the lattice distortion is much larger than the resistance due to the extra ion.

These calculations were refined by Overhauser and Gorman (1956), who analyzed the displacements into Fourier components and calculated the resulting resistivity from the interaction between electrons and short lattice waves, as deduced from the high temperature resistance. The resistance due to distortions turned out to be even larger than estimated by Jongenburger, while interference between the lattice distortion and scattering by the extra ion turned out to be unimportant.

DISLOCATIONS

In the case of extended imperfections, scattering is due to the displacements. In the case of a dislocation, the position of the atoms is known, but in order to define the unperturbed lattice, one must go very far away from the dislocation. It is therefore best to abandon the concept of displacements as a source of scattering. It was pointed out by Hunter and Nabarro (1953) that a uniform displacement and a uniform strain do not lead to scattering, but that scattering is due to inhomogeneous strains.

One can thus resolve the strain into Fourier components and treat the scattering of electrons by such a strain field in an analogous manner to the scattering by lattice vibrations. The rate of change of the electron distribution function due to phonons is given by

$$t \frac{df}{dt} = \frac{2}{9MG\hbar} \sum_{\mathbf{q}, j} C_j^2 \frac{q^2}{\omega} \Omega(\Delta E) [f'(1-f)(N+1) - (1-f')fN]$$

where

$$\Delta E = E + \hbar\omega - E',$$

$$\Omega(\Delta E) = 2 \frac{1 - \cos(\Delta E t / \hbar)}{(\Delta E / \hbar)^2},$$

and M is mass of unit cell, G number of unit cells.

We estimate C^2 from the low temperature thermal resistivity in preference to the electrical resistivity, for the latter is somewhat sensitive to details of the band structure. Another estimate can be made from the magnitude of the lattice thermal conductivity. We find that

(a) there is equal interaction between electrons and waves of all polarizations,*

(b) for copper $(C/\xi)^2 \sim 0.1$.

In the case of static strain fields, the expression must be rewritten in terms of the amplitudes

$$a_{\mathbf{q}} = \left\{ \frac{\hbar}{2M\omega} \left(\frac{N}{N+1} \right) \right\}^{\frac{1}{2}}.$$

If the strain field is decomposed into Fourier components

for dilatation
$$\Delta(\mathbf{x}) = \frac{1}{\sqrt{G}} \sum_{\mathbf{q}} D(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}),$$

for rotation
$$\Pi_i(\mathbf{x}) = \frac{1}{\sqrt{G}} \sum_{\mathbf{q}} P_i(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}),$$

then one can identify $qa_{\mathbf{q}}$ with $D(\mathbf{q})$ for longitudinal waves, and with $P(\mathbf{q})$ for transverse waves. Thus

$$i \frac{df}{dt} = \frac{4C^2}{9\hbar^2 G} \sum_{\mathbf{q}} \left\{ \sum_i P_i^2(\mathbf{q}) + D^2(\mathbf{q}) \right\} \Omega(\Delta E) [f' - f].$$

This expression is formally equivalent to that occurring in the theory of the scattering of phonons by static strain fields (Klemens 1955), and in a similar way we get

$$\frac{1}{\tau} = \frac{2\pi}{9} (0.55) \frac{C^2}{\hbar^2} N b^2$$

for the relaxation time due to N screw dislocations per unit area, of Burgers vector b , and a similar expression for edge dislocations.

In the case of copper

$$1/\tau = 0.24 N$$

and at room temperature

$$\Delta\rho/\rho = 6.3 \times 10^{-15} N.$$

This calculation is, of course, similar in principle to that of Hunter and Nabarro, differing mainly in the strength of the interaction assumed. These authors estimated the interaction parameter C for dilatation and shear from first principles, and obtained

$$\Delta\rho/\rho = 2.1 \times 10^{-15} N.$$

Both these calculations can be criticized for being based on elastic continuum theory. Most of the scattering arises at a distance of about one wavelength

*See discussion following Bardeen's paper, also Klemens (1956).

away from the dislocation line. In the case of the scattering of low frequency phonons this means that the scattering is insensitive to the structure of the dislocation core, but in the case of electrons the opposite is true. Most of the scattering arises from the immediate vicinity of the dislocation line, and a reliable theory would have to take detailed account of the structure of the dislocation core.

STACKING FAULTS

The same formalism can be used to obtain the scattering by a stacking fault. The stacking fault is represented by a strong but localized shear. A detailed calculation for copper gave a value of 0.4 for the probability of specular reflection. This estimate gives us only the order of magnitude, because perturbation theory must break down for such high scattering probabilities. It does, however, lend support to an earlier estimate (Klemens 1953) based on a wave-fitting calculation on the assumption of strong departure from the free electron model, which yielded a scattering probability of 0.5.

COMPARISON WITH OBSERVATIONS

A great deal of work has been done on the electrical resistance changes produced by irradiation and plastic deformation, mainly in copper. This work has been reviewed by van Bueren (1955) and Seeger (1956). Five annealing stages have been observed, each one presumably corresponding to the disappearance of one type of imperfection. It appears that the resistance due to dislocations is larger than expected, if the density of dislocations is taken from stored energy data.

This view was confirmed by work on the simultaneous measurements of lattice thermal conductivity and electrical resistance in plastically deformed copper alloys, recently carried out in Sydney by Kemp, Tainsh, and White. In all these cases it was found that phonons were strongly scattered by dislocations introduced by deformation. In the case of Cu-Zn alloys, plastic deformation also introduced point imperfections. From the magnitude of the point-imperfection scattering, it appeared likely that the bulk of the additional electrical resistance is due to point imperfections. It also appears that the point imperfections are small vacancy clusters. But in the case of an arsenical copper specimen, identical to that used by the Melbourne group in their stored energy studies (Clarebrough, Hargreaves, and West 1955), and deformed in the same way, it appears that deformation produces dislocations, but there is no appreciable increase in the scattering of phonons by point imperfections. Assuming that the electrical resistance increase is due to dislocations, and using the dislocation resistance calculated here, one finds $N \sim 6 \times 10^{12} \text{ cm}^{-2}$ for the dislocation density. This is in agreement with the estimate from the phonon scattering ($N \sim 8 \times 10^{12}$), but disagrees violently with estimates from stored energy ($N \sim 0.2 \times 10^{12}$). It is possible that stored energy estimates are systematically in error, especially as they contain a logarithmic dependence on crystal size, but if they are not, then there is a systematic error in the scattering by dislocations both of electrons and phonons. Since different wavelengths are involved, this is somewhat puzzling.

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DISCUSSION OF KLEMENS'S PAPER

Pines: You took $(C/\tau)^2 \sim 0.1$ for copper. Is not this value of C excessively small? Theoretical considerations lead to a larger value of C , as do resistance data.

Klemens: This is the value of C derived from the low temperature ideal *thermal* resistivity. It is less than the usually accepted empirical values because: (a) the high temperature resistivity appears to be too high relative to the low temperature thermal resistivity and (b) C^2 is reduced by a factor 3 because equal interaction with modes of all polarizations was assumed.

Ziman: In estimating C^2 from the low temperature thermal resistivity, did you take account of Umklapp processes?

Klemens: No, because only electrons on a small fraction of the Fermi surface can undergo these Umklapp processes.

Mott: I think that there are other people here who have views on the scattering of stacking faults.

Ziman: Tweedale of the Cavendish Laboratory has attacked this problem by matching the electron wave functions on either side of the boundary. He estimates the reflection coefficient to be of the order of 10^{-4} in copper.

Mott: How specific is his model?

Ziman: It is a model for copper, but not a very close one. The calculation also gives the right order of magnitude for the energy of the stacking fault: 100 ergs cm.⁻², compared with an observed energy of 40 ergs cm.⁻². Now the reflection coefficient is measured at the Fermi surface, and if it does not vary too rapidly through the Fermi distribution one would expect there to be a relation between the reflection coefficient and the energy of the stacking fault. While this may not be too precise, it would be surprising if any reasonable model could lead to an error of 10^4 in this relation.

Mott: The stacking fault energy is sensitive to atomic structure, and is greater for crystals of divalent atoms. Does anyone know if there are any indications that the reflection coefficient is correspondingly greater?

Seeger: Preliminary investigations we have carried out at Stuttgart show that this whole matter is rather complicated. I shall go into this in more detail in my paper. Our result for the reflection coefficient of a stacking fault is in

rough agreement with Dr. Klemens's, but it is based on a perturbation method that is certainly not rigorous. However, it seems rather unlikely that reflection coefficient and stacking-fault energy are directly related.

Nabarro: If scattering by stacking faults is large, there will be a large anisotropy of magnetoresistance for different directions of the magnetic field which all lie perpendicular to the dislocation line. If **B** is perpendicular to the glide plane, the circular electron orbits will not intersect the stacking fault, while if **B** is in the glide direction, there will be scattering by the stacking fault. This anisotropy should much exceed the anisotropy of the ordinary resistance, which is 3:1 according to most calculations, and even less according to recent ideas of Seeger. It could best be detected by measurements on a bent single crystal. I do not know if this question is answered by the existing experiments of van Bueren.

Seeger: Calculations are in progress at Stuttgart on the magnetoresistivity of extended dislocations (containing a stacking-fault ribbon).

ON THE ELECTRICAL RESISTIVITY OF STACKING-FAULTS IN MONOVALENT METALS^{1,2}

BY ALFRED SEEGER³

1. INTRODUCTION AND SURVEY OF THE EXPERIMENTAL SITUATION

The problem of the electrical resistivity or the reflection coefficient for conduction electrons of a stacking-fault in a metal, say in copper, is a particularly interesting one at the present moment. Experimental evidence on the increase of resistivity of cold-worked copper due to dislocations, which will be reviewed below, indicates that the reflection coefficient of a stacking-fault must be rather high, of the order of 1/10 to 1. On the other hand there is at least equally strong evidence that the specific free energy of a stacking-fault γ in monovalent metals is rather small, a generally accepted value for copper being $\gamma = 40$ ergs/cm.² (Seeger and Schöck 1953).^{*} If we ascribe to the stacking-fault a thickness d of two atomic layers ($d = 2c = 2a/\sqrt{3}$; a = length of cube edge), $\gamma = 40$ ergs/cm.² corresponds to an increase of the energy per atom of 2×10^{-3} of the cohesive energy per atom, which is a very small fraction indeed. The conclusions to be drawn from this are that a stacking-fault increases the energy of the electrons in a monovalent metal only very slightly but is nevertheless an effective scatterer of conduction electrons, and that the energy and reflection coefficient of a stacking-fault are not directly related to each other. Direct experimental evidence for the last statement will be quoted below.

In order to determine the (average) electrical resistance per unit length of a dislocation line we require, in addition to the measurement of the resistivity due to dislocations in a cold-worked specimen, the knowledge of the (bulk) density of dislocations. Estimates of the density of dislocations after cold-work can be obtained from measurements of the stored energy, the change in density, and the flow-stress. Simultaneous measurements of the resistivity, the stored energy, and the change of density of cold-worked polycrystalline copper and nickel, have been published by Clarebrough, Hargreaves, and West (1955) and discussed in the light of theory by Seeger and Stehle (1956). It was shown that the ratio of the change of the stored energy to the change of density in the recovery stages due to the disappearance of dislocations agreed rather well with theory. It seems therefore to be justified to base the discussion of dislocation resistivity on a comparison between the

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The calculations reported in this paper have been done in cooperation with Dipl. Phys. H. Stehle. The responsibility for the present form of the manuscript rests solely with the present author. He would like to thank Dipl. Phys. H. Stehle for many stimulating discussions.

²*Editor's note:* This paper was written after the conference, and thus includes part of the material of the subsequent discussion. There is, therefore, a certain amount of duplication.

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^{*}For the evidence on stacking-fault energies see Seeger (1955a).

change in density (and/or the stored energy released during annealing) and the corresponding change in electrical resistivity. This is a particularly suitable procedure since theory shows (Seeger and Stehle 1956; Stehle and Seeger 1956) that the electrical resistivity of an unextended dislocation in a monovalent metal is related, though not exactly proportional, to the increase of volume due to a dislocation.* The dislocation resistivity per 1% of volume expansion should therefore not be too sensitive to the detailed arrangement of the dislocations, which is unknown in the case of the Clarebrough, Hargreaves, and West experiments.

Table I (taken from Seeger and Stehle (1956)) compares the experimental data with those calculated for unextended dislocations. The theoretical value

TABLE I
RATIO OF DISLOCATION RESISTIVITY TO CHANGE IN
SPECIFIC VOLUME DUE TO DISLOCATIONS (ALL NUMBERS
ARE GIVEN IN $\mu\Omega\text{-CM.}/\%$ INCREASE IN VOLUME)

	Theoretical	Experimental
Cu	0.06	2.5
Ni	0.18	10

for nickel is an estimate based on experimental and theoretical values for the resistivity of vacancies in nickel.

From Table I it is apparent that a large discrepancy exists between experiment and theory: the experimental dislocation resistivity in both copper and nickel is about 40 times larger than the theoretical value.

A similar discrepancy is obtained by comparing the change in flow-stress with the change in resistivity during cold-work. Since the flow-stress is somewhat sensitive to the details of the dislocation arrangement, it is more difficult to express the discrepancy numerically.

The reason why this discrepancy is genuine and not just due to a misinterpretation of experimental data has been given elsewhere (Seeger and Stehle 1956) and will not be reported here. Two possible explanations have been proposed to account for the discrepancy. It was proposed by Mott and worked out in some detail by Stroh (1956) that on the dilatation side of an edge dislocation a wedge-shaped crack should form and contribute to the increase in volume and resistivity due to a dislocation. Boas (1956) however showed that in order to account for the experimental results these cracks would have to be so large that they should be easily visible, contrary to what is observed. This explanation can therefore be ruled out.

Stehle and Seeger (1956) considered crack formation at edge dislocations to be unlikely in metals as ductile as copper and nickel. Their final conclusion

*It might be mentioned in passing that volume increase caused by a dislocation is a non-linear effect, which is not contained within the framework of Hookeian elasticity. The large strains in the environment of a dislocation line cause a net expansion of the crystal near the dislocation line, which in turn causes a transfer of electrons from the less-expanded outer region to the dislocation center. The corresponding potential scatters electrons rather effectively and gives a substantial contribution to the total dislocation resistance.

was (Seeger and Stehle 1956) that it was not justified in the cases considered to treat the dislocations as being unextended, but that an essential contribution to the resistivity of cold-worked noble metals came from stacking-faults (which are present in the stacking-fault ribbons of extended dislocations) as first proposed by Broom (1952) and later discussed by other authors, e.g. Koehler (1955). This conclusion was substantiated by a discussion of the (rather meager) experimental data available for aluminum, the dislocations in which are known to have rather narrow stacking-fault ribbons only.

The implication of this interpretation is that the reflection coefficient R of a stacking-fault in a noble metal must be rather large, being not more than one order of magnitude smaller than unity. As already mentioned this means that stacking-fault resistivity and stacking-fault energy γ are not directly related to each other. There is direct experimental evidence that not even for very small values of γ , where these two quantities might be expected to be proportional to each other, does the stacking-fault resistivity depend markedly on γ . Near the phase-boundary between the cubic and the hexagonal close-packed phase of the binary alloy Ni-Co the stacking-fault energy must become small compared with that of pure nickel, which is thought (Seeger 1955*b*) to be of the order $\gamma = 80$ ergs/cm.² In this region of stacking-fault energies the width of the stacking-fault ribbon will be inversely proportional to γ . If the reflection coefficient were proportional to γ the resistivity of an extended dislocation would be independent of the stacking-fault energy and no anomaly of the electrical resistivity of cold-worked Ni-Co alloys would be expected. Broom and Barrett (1953), however, have observed that near the phase-boundary cold-worked Ni-Co alloys show a very pronounced maximum of the increase in electrical resistivity as a function of the concentration. It seems unlikely that a change in the deformation mechanism could be responsible for all the observed additional resistance.* The conclusion is that the reflection coefficient of the stacking-faults remains high even when the stacking-fault energy becomes small.

2. SURVEY OF THE THEORETICAL SITUATION

The calculation of the reflection coefficient of a stacking-fault, even in a monovalent metal, appears to be a rather formidable problem. The principal reason for this is that none of the methods developed for treating electron scattering by static imperfections is applicable to the stacking-fault problem. For example, it is obvious that in the free-electron approximation (in which the potential is assumed to be constant inside the metal) electrons do not feel the presence of a stacking-fault at all. The reduction of the real problem, involving a periodic lattice potential and Bloch-type wave functions, to a free-electron problem by means of the Wannier-Slater approximation, which is very useful in impurity scattering (Friedel 1954), is therefore inapplicable. The approximation developed for slowly varying strains (Bardeen's and Shockley's (1950) method of deformation potentials, further developed by Hunter

*Experiments on the plastic deformation of Ni-Co single crystals are in progress at Stuttgart and are expected to have a bearing on this point.

and Nabarro (1953)) cannot be employed either, since a stacking-fault contributes a very localized strain of order unity in an otherwise unstrained crystal.

The fact that the usual approximations do not work in the stacking-fault problem means that in order to obtain a reliable answer one has to work out a rather complete solution of the problem. We shall outline below qualitatively the nature of such a solution. At the present time it has not yet been worked out quantitatively. All available calculations of stacking-fault reflection coefficients are order-of-magnitude estimates only. There are large discrepancies between the various estimates; we will briefly review the main ideas involved and the results obtained.

The earliest estimate was produced by Klemens (1953), which gave the rather large reflection coefficient $R = \frac{1}{2}$ for an electron with perpendicular incidence. The basis of the estimate was the assumption that when passing through the stacking-fault the Bloch wave $\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ (or rather the exponential factor e^{ikz}) undergoes a phase shift corresponding to the relative displacement of the atoms on opposite sides of the stacking-fault. A localized potential which gave this phase-shift was introduced, and from the relative intensity of the reflected wave the reflection coefficient was found.

Blatt (1956; Blatt, Ham, and Koehler 1956) has pointed out that this procedure suffers from the obvious drawback that a large reflection coefficient is obtained also for free electrons for which it is known to be zero. A further objection is that the potential-well introduced in order to give the phase-shift and the reflected wave will give rise to a stacking-fault energy much larger than the observed one.

Very recently Klemens (1956) estimated $R = 0.4$ by treating the shear in the stacking-fault (which has the character of a δ -function) by the Hunter-Nabarro method. We have already remarked that this use of the deformation potential method goes far beyond its range of applicability, so that it is hard to assess the accuracy of the numerical result.

Before mentioning further theoretical treatment it is helpful to discuss the qualitative nature of what we have called the complete solution. It is clear that far away from the stacking-fault the correct one-electron wave-functions are the same as those in a crystal without a stacking-fault (or rather linear combinations of the Bloch-functions of the periodic lattice). If as a first approximation we consider the two half-crystals on both sides of the stacking-fault to be displaced rigidly with respect to each other, bound states analogous to the well-known Tamm surface states (or to the Rayleigh waves in the mechanics of continua) will be necessary in order to satisfy the continuity conditions at the stacking-fault. The charge distribution connected with these exponentially decaying bound-state wave-functions will to some extent change the potential in each of the half-crystals. This in turn leads to a modification of both the Bloch-type and Tamm-type parts of the one-electron wave-function. The "complete" solution can evidently be arrived at by a self-consistent field method. However it is thought that the self-consistent potential differs only slightly from the potential obtained by displacing the half-crystals

rigidly with respect to each other. The argument is as follows: If the electrostatic field of each ion-core were shielded completely by the conduction electrons within its atomic cell the electrostatic potential would be exactly the one that is obtained by treating the half-crystals as being rigid. The extra potential that arises from a charge redistribution near the plane of the stacking-fault is determined by the overlap of the ion-core field into neighboring atomic cells and is reduced by the tendency of the conduction electrons to screen out any deviation from the potential of the ideal crystal. The remaining deviations will give rise to an increase in the energy of the conduction electrons, which however cannot be larger than the stacking-fault energy. The order of magnitude of the effective scattering cross-section at the Fermi surface and the resistivity due to such a perturbing potential can be estimated from the corresponding energy increase and is found to be very small in the present case since the stacking-fault energy is so small. For many purposes we may therefore forget about this extra potential and treat the two halves of the crystal as rigid.

A practical starting point for the self-consistent procedure outlined above would be to match across the stacking-fault plane the Bloch-function of a given energy and the corresponding Tamm-function, which are modulated plane-waves along the stacking-fault plane, decaying exponentially in the directions perpendicular to the stacking-fault. Function-matching techniques have been used by Blatt, Ham, and Koehler (1956)* and by Tweedale (see the contributions of J. Ziman to the discussions of this paper and of Klemens's). Blatt, Ham, and Koehler use the Bardeen (1938) version of the Wigner-Seitz method. The matching was done at one point on the surface of each Wigner-Seitz sphere only. Tweedale used the augmented plane wave method (for a description, see Reitz (1955)) and could do the matching somewhat more completely. In both investigations however the Tamm waves were not taken into account. The electrical resistivity of the stacking-fault in an extended dislocation in copper was found to be small compared with the resistivity of the partial dislocation bordering it. Tweedale estimates that the reflection coefficient is of the order 10^{-3} to 10^{-4} .

The theoretical results just quoted are not in line with the experimental results as outlined in §1. We believe that the two calculations based on function matching just mentioned give much too small a value for the coefficient of reflection. It is thought that this is due to the fact that in both matching procedures the surface waves have not been considered and that the matching is necessarily incomplete.

Another way of looking at the scattering of electrons by stacking-faults is to consider it as a diffraction phenomenon. Whereas in the usual electron diffraction experiments a plane wave may be diffracted when entering the region of the periodic potential inside the crystal, in the present case a modulated plane-wave (Bloch-function) is scattered when passing from one periodic medium to another one with different characteristics. We shall see in the next paragraph that this can give rise to a rather large reflection coefficient.

*The author is grateful to Dr. Blatt for sending him a detailed manuscript of this paper.

Looking at the electrical resistance of a stacking-fault as being due to a diffraction phenomenon helps to remove the difficulty of a large reflection coefficient going together with a small stacking-fault energy. Scattering of the boundary of two perfect crystals will not change the energy of the Bloch waves very much, and an increase in energy in some direction of the \mathbf{k} -space will be compensated partially by a decrease in others.

Qualitatively the diffraction approach seems to be capable of explaining the main experimental facts on stacking-faults in copper. We shall develop the calculation of the electrical resistivity along these lines in §3.

3. THEORY OF THE ELECTRICAL RESISTIVITY OF STACKING-FAULTS IN MONOVALENT METALS

3.1. Outline

The usual approach to the theory of electron diffraction by crystals is the geometrical or kinematical theory, which is equivalent to perturbation theory. It is known that it breaks down for electrons whose kinetic energy is comparable with the Fermi energy. This means that in the present case the application of this type of theory, which allows us to obtain explicit results, needs special justification. This can be done as follows: Let us consider a "model crystal", the periodic potential in which is so smooth that it can be considered as a "small perturbation" to an electron at the Fermi surface of a monovalent metal. The potential inside the crystal will then be almost constant and the Bloch-functions will very nearly be plane waves. Since free electrons (corresponding to a constant potential inside the metal) are not scattered by a stacking-fault, we will certainly not overestimate the reflection coefficient of the model crystal as compared with that of the real metal. The calculations in §3.3 show that, even in our model crystal, in nearly all directions of \mathbf{k} -space there is strong scattering by a stacking-fault. This is contrary to what is known for electrons entering the crystal from outside where appreciable scattering occurs only for electrons with \mathbf{k} -vectors near the boundary of a Brillouin zone. Strong reflection and a large electrical resistivity is therefore expected for stacking-faults in real crystals, the details depending on the exact nature of the periodic potential. An estimate of some of the quantities involved can be obtained without explicit reference to the lattice potential; they should be useful also in the range where perturbation theory is doubtful.

3.2. High and Low Temperature Resistivity of Anisotropic Static Scatterers

For use in later sections we give here a few results of the formal theory of electronic conduction in metals. The basic assumption we start from is that the conduction electrons are quasi-free, i.e., their one-electron energies are given by

$$(1) \quad \epsilon = (\hbar^2/2m^*)k^2$$

($2\pi\hbar$ = Planck's constant, $k = |\mathbf{k}|$ = modulus of wave-vector of electron). m^* is the effective mass of the conduction electrons; it may be treated as a scalar quantity in unstrained cubic metals. Eq. (1) has to be rewritten for non-cubic metals, and also for homogeneously strained cubic metals, in order

to allow for the tensor character of $1/m^*$. It is standard practice to use Eq. (1) for all cubic *monovalent* metals, although it is known that in these metals the Fermi surfaces do deviate somewhat from the spherical shape implied by Eq. (1). As was shown elsewhere (Seeger 1956a) the calculation of electrical resistivity of static lattice imperfections based on equation (1) may also be applied to ferromagnetic nickel and some related materials.

If the energy surfaces are spherical as implied by Eq. (1) and if the collisions of the electrons are elastic, we are justified in using relaxation times. The second condition is satisfied either above the Debye temperature or at temperatures sufficiently low to neglect the thermal scattering compared with that due to static imperfections. Since the scattering of electrons by static imperfections like dislocations and stacking-faults is anisotropic, i.e., depends on the orientation of the \mathbf{k} -vector of the incident electron with respect to the scattering imperfection, the relaxation time τ_{st} due to static scattering must be treated as a tensor quantity.

The relation between the total relaxation time τ and the relaxation time τ_{th} due to thermal scattering (which we consider to be isotropic, i.e., depending on the angle between the wave vector of the incident and the outgoing wave only and not on the orientation of the wave vectors relative to the crystal structure) is as follows:

At low temperatures

$$(2) \quad \tau = \tau_{st}.$$

At high temperatures where τ_{st} is always large compared with τ_{th} :

$$(3) \quad \frac{1}{\tau} = \frac{1}{\tau_{th}} + \frac{1}{\tau_{st}}$$

or approximately

$$(3a) \quad \tau = \tau_{th} - \frac{\tau_{th}^2}{\tau_{st}}.$$

It is also standard practice to employ the Boltzmann equation which says that the rates of change of the distribution function $f(\mathbf{k})$ of the electrons (in equilibrium $f = f_0$) due to the applied electric field \mathbf{F} and due to the collisions of the electrons should make the distribution stationary, i.e.

$$(4) \quad \left. \frac{\partial f}{\partial t} \right|_{field} + \left. \frac{\partial f}{\partial t} \right|_{coll} = 0.$$

We have

$$(5) \quad \left. \frac{\partial f}{\partial t} \right|_{field} = \frac{d\mathbf{k}}{dt} \cdot \text{grad}_{\mathbf{k}} f \approx -\frac{e\mathbf{F}}{\hbar} \cdot \mathbf{k} \frac{\partial f_0}{\partial \epsilon} \frac{\hbar^2}{m^*}$$

(e = modulus of elementary charge) and

$$(6) \quad \left. \frac{\partial f}{\partial t} \right|_{coll} = \iint [f(\mathbf{k}) - f(\mathbf{k}')] P(\mathbf{k}, \mathbf{k}') dS'$$

where $P(\mathbf{k}, \mathbf{k}')$ is the probability per unit time of an electron being scattered

from a state \mathbf{k}' to a state \mathbf{k} and the integral is to be extended over the Fermi surface. The (symmetrical) second-order relaxation time tensor τ is introduced by the equation

$$(7) \quad f = f_0 - \frac{e\hbar}{m^*} \frac{\partial f_0}{\partial \epsilon} \mathbf{F} \cdot \boldsymbol{\tau} \cdot \mathbf{k}$$

which, for a scalar τ , is equivalent to the well-known "Ansatz"

$$(7a) \quad \left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = -\frac{f - f_0}{\tau}.$$

We shall give the formulae for the additional electrical resistivity $\Delta\rho$ of two types of anisotropic scatterers in which only one component of the τ_{st} tensor is relevant.

(a) *Cylindrical Symmetry of the Scattering Potential (e.g., Screw Dislocation Running along z-Direction)*

$$(8) \quad \begin{cases} \tau_{ss} = \infty, \\ \tau_{zz} = \tau_{yy} = \tau_{st}, \\ \tau_{zy} = \tau_{yz} = \tau_{yz} = \tau_{zy} = \tau_{zx} = \tau_{xz} = 0. \end{cases}$$

High temperatures (above Debye temperature):

$$(9) \quad \Delta\rho = \frac{m^*}{e^2 n_0} \overline{\tau}^{-1},$$

$$(9a) \quad \overline{\tau}^{-1} = \frac{3}{4} \int_{-1}^{+1} \frac{(1-\xi^2)}{\tau_{st}(\xi)} d\xi.$$

Low temperatures:

$$(10) \quad \Delta\rho = \frac{m^*}{e^2 n_0} \frac{1}{\overline{\tau_{st}}},$$

$$(10a) \quad \overline{\tau_{st}} = \frac{3}{4} \int_{-1}^{+1} (1-\xi^2) \tau_{st}(\xi) d\xi.$$

In these formulae n_0 is the number of conduction electrons per unit volume and $\xi = k_z/k_F$, the ratio between the z -component and the modulus of the wave-vector \mathbf{k} at the Fermi sphere. τ_{st} can be expressed by the phase-shifts $\eta_n(\xi)$ of an electron scattered by the cylindrical potential as follows:

$$(11) \quad \frac{1}{\tau_{st}(\xi)} = \frac{4\hbar}{m^*} \sum_{n=-\infty}^{n=+\infty} [\sin \eta_n \cos \eta_{n+1} \sin(\eta_n - \eta_{n+1})].$$

For more details concerning the electron scattering by a potential of circular cylindric symmetry, in particular by a screw dislocation, see Stehle and Seeger (1956) and Seeger and Stehle (1956).

(b) *Stacking-fault (Lying in x-y Plane)*

$$(12) \quad \begin{cases} \tau_{zz} = \tau_{st}, \\ \tau_{xx} = \tau_{yy} = \infty, \\ \tau_{xy} = \tau_{yz} = \tau_{yz} = \tau_{xy} = \tau_{xz} = \tau_{zx} = 0. \end{cases}$$

For high temperatures Eq. (9) holds with

$$(9b) \quad \tau^{-1} = \frac{3}{2\pi} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \frac{\cos^2 \theta \sin \theta d\theta d\phi}{\tau(\theta, \phi)}$$

whereas at low temperatures Eq. (10) with

$$(10b) \quad \bar{\tau} = \frac{3}{2\pi} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \tau(\theta, \phi) \cos^2 \theta \sin \theta d\theta d\phi$$

applies. Here θ and ϕ are the angles of incidence according to Fig. 1. The x -direction is taken to be the direction of the displacement vector \mathbf{b} of the stacking-fault. An expression for $\tau(\theta, \phi)$ will be given below.

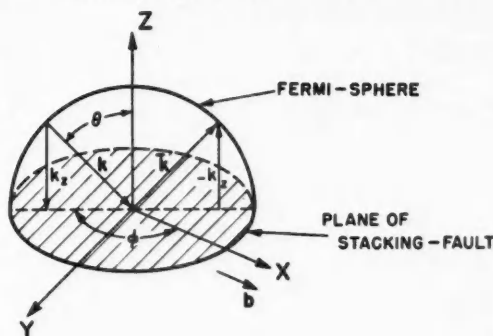


FIG. 1. Reflection of an incident electron with wave-vector \mathbf{k} by a stacking-fault. The reflected wave-vector is $\mathbf{k}' = \bar{\mathbf{k}}$.

It is easy to see that an unbounded stacking-fault may be described by a reflection coefficient $R(\theta, \phi)$ depending on the direction of incidence. The x - and y -components of the wave-vector remain unchanged during the scattering of an electron; in order to preserve the energy of the scattered electron (i.e., keeping its wave-vector on the Fermi surface) the z -component k_z must either be preserved (in which case there is no scattering at all) or changed into $-k_z$. The wave-vector with components $k_x, k_y, -k_z$ will be denoted by $\bar{\mathbf{k}}$. The scattering from \mathbf{k} to $\bar{\mathbf{k}}$ corresponds to optical reflection.

If A/V denotes the stacking-fault area per unit volume the rate at which an electron is scattered from \mathbf{k} to $\bar{\mathbf{k}}$ is given by

$$v_z R[f(\mathbf{k}) - f(\bar{\mathbf{k}})] \cdot A/V$$

where v_z is the velocity component perpendicular to the stacking-fault and R is the reflection coefficient of the stacking-fault. Making use of the symmetry relation $\tau(\theta, \phi) = \tau(\pi - \theta, \phi)$ we obtain from Boltzmann's equation the following relation between $\tau(\theta, \phi)$ and the reflection coefficient:

$$(13) \quad \frac{1}{\tau(\theta, \phi)} = 2 \cos \theta \frac{\hbar k_F}{m^*} R(\theta, \phi) \cdot A/V.$$

Eq. (13) can only be approximately valid since $\tau = 0$ should correspond to $R = 1$. R. Landauer (private communication) has pointed out the deficiency

of Eq. (13) in relation to the fact that no attention has been paid to the spatial variation of the distribution function near the scatterer. If this is done an impenetrable plane obstacle ($R \equiv 1$) does indeed give a zero relaxation time.

In concluding this section we should like to make a few remarks on the interrelation between the formulae we have derived for high and for low temperatures. They agree only if τ_{st} is a constant. That means that an anisotropic scatterer always gives rise to deviations from Matthiessen's rule. Formulae (9) and (10) show that, in the cases we have considered, the resistivity at high temperature is an average over the resistivity contributions of those parts of \mathbf{k} -space which do not mix on scattering, whereas the average at low temperature is made over the contributions to conductivity. One may speak of resistors being in parallel or series in \mathbf{k} -space. This brings out at once the well-known result that, if there are deviations from Matthiessen's rule, the high temperature resistivity of a static imperfection is larger than the low temperature resistivity (so-called positive deviation from Matthiessen's rule). For a further discussion of the deviation from Matthiessen's rule due to dislocations, based on Eqs. (9a) and (10a), see Seeger and Stehle (1956).

3.3. Scattering of Electrons by Stacking-faults

As we have already indicated in §3.1, we are going to calculate the electrical resistivity of a stacking-fault by perturbation theory. Wilson (1953) gives the following formula for the rate of change of the distribution function due to collisions:

$$(14) \quad \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} = \frac{m^* \Omega}{4 \pi^2 \hbar^3 k_F V} \iint (f(\mathbf{k}) - f(\mathbf{k}')) |(\mathbf{k} | V^p | \mathbf{k}')|^2 dS'.$$

The meaning of the symbols is as follows: Ω is the atomic volume, V is the total volume of the crystal, k_F is the modulus of the wave-vector at the Fermi sphere. The integration in Eq. (14) has to be carried out over the Fermi surface. $(\mathbf{k} | V^p | \mathbf{k}')$ is the matrix element of the perturbing potential V^p , taken over the entire crystal volume V . We have written Eq. (14) in such a way that the Bloch-type wave-function

$$(15) \quad \psi_{\mathbf{k}} = u_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

entering into the matrix element

$$(16) \quad (\mathbf{k} | V^p | \mathbf{k}') = \iiint_{\text{crystal}} \psi_{\mathbf{k}}^* V^p \psi_{\mathbf{k}'} d\tau$$

is normalized within one atomic cell according to

$$(16a) \quad \iiint_{\text{cell}} \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} d\tau = 1.$$

We characterize each atomic cell by a position vector

$$(17) \quad \mathbf{r}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

and put

$$(17a) \quad \mathbf{k} - \mathbf{k}' = \mathbf{h} = h_1 \mathbf{p}_1 + h_2 \mathbf{p}_2 + h_3 \mathbf{p}_3$$

where

$$(17b) \quad \mathbf{a}_i \mathbf{p}_k = 2\pi \delta_{ik}.$$

If $V_L(\mathbf{r})$ denotes the periodic lattice potential acting on the conduction electrons and \mathbf{b} the displacement vector of the stacking-fault, we may write for the perturbing potential

$$(18) \quad V^p(\mathbf{r}) = \begin{cases} 0, & -N_1 \leq n_1 \leq N_1, -N_2 \leq n_2 \leq N_2, -N_3 \leq n_3 \leq -1; \\ -V_L(\mathbf{r}) + V_L(\mathbf{r} + \mathbf{b}), & -N_1 \leq n_1 \leq N_1, -N_2 \leq n_2 \leq N_2, \\ & 0 \leq n_3 \leq N_3. \end{cases}$$

In Eq. (18) we have neglected the fact that the shielding of the ion potential may not be quite complete within one unit cell. This will cause some deviation from Eq. (18) in the neighborhood of the stacking-fault. The effect of this deviation on the electrical resistivity at high temperature will be small, as indicated already in §2.

Inserting Eq. (18) in Eq. (16) we can carry out the summation over the atomic cells of the crystal and obtain

$$(19) \quad |(k|V^p|k')|^2 = |V_c|^2 \frac{\sin^2 \pi h_1 (2N_1 + 1)}{\sin^2 \pi h_1} \cdot \frac{\sin^2 \pi h_2 (2N_2 + 1)}{\sin^2 \pi h_2} \cdot \frac{1 - \cos 2\pi h_3 (N_3 + 1)}{1 - \cos 2\pi h_3}$$

where

$$(20) \quad V_c = \iiint_{\text{cell}} u_{\mathbf{k}} u_{\mathbf{k}'}^* V^p e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} d\tau$$

is the matrix element taken for one cell. We have further

$$(21) \quad \begin{cases} \pi h_3 = c k_F \cos \theta, \\ \pi h_1 = \frac{1}{2}(k_x - k_x') \cdot c, \\ \pi h_2 = \frac{1}{2}(k_y - k_y') \cdot c, \\ \frac{1 - \cos 2\pi h_3 (N_3 + 1)}{1 - \cos 2\pi h_3} = \frac{\sin^2 [c k_F \cos \theta (N_3 + 1)]}{\sin^2 (c k_F \cos \theta)}. \end{cases}$$

$c = a/\sqrt{3}$ is the separation between $\{111\}$ -planes in a face-centered cubic crystal. Putting $dS' = dk_x' dk_y' / \cos \theta$, the integration in Eq. (14) can be carried out if N_1 and N_2 are considered to be very large numbers. Inserting the result into Boltzmann's equation we obtain finally

$$(22) \quad \frac{1}{\tau(\mathbf{k})} = \frac{2}{\tau(\mathbf{k}) + \tau(\mathbf{k})} = \frac{2 m^* \Omega}{\hbar^3 k_F c^2 A_0} V \cdot |V_c|^2 \frac{1}{\cos \theta} \frac{\sin^2 [c k_F \cos \theta (N_3 + 1)]}{\sin^2 [c k_F \cos \theta]}$$

where

$$(22a) \quad A_0 = \frac{1}{4} a^2 \sqrt{3}$$

is the area per atom on the stacking-fault plane. According to Eq. (22) the relaxation time of a stacking-fault is a rapidly varying function of the angle θ between the incident wave-vector \mathbf{k} and the direction normal to the stacking-

fault. The period of the oscillation is the smaller, the more atomic layers are behind the stacking-fault. This was to be expected since we are dealing with a diffraction phenomenon. For many purposes we may replace the rapidly varying factor $\sin^2[c k_F \cos \theta (N_3 + 1)]$ by its average value $\frac{1}{2}$, except for very small value of $\cos \theta$, i.e., nearly glancing incidence. Making use of Eq. (13) we obtain for the reflection coefficient with these simplifying assumptions

$$(23) \quad R = \frac{1}{2} \cdot \frac{(m^*)^2 \Omega}{\hbar^4 k_F^2 c A_0^2} \frac{1}{\cos^2 \theta} |V_c|^2 \frac{1}{\sin^2(c k_F \cos \theta)}.$$

Since in general V_c will not tend to zero for $\cos \theta \rightarrow 0$, Eq. (23) gives a reflection coefficient larger than unity for small $\cos \theta$. This was discussed above and is due to the assumption made in treating Boltzmann's equation. Presumably R will be of the order $\frac{1}{2}$ for nearly glancing incidence. For no direction of \mathbf{k} must R be larger than unity. Since R fluctuates between one and zero, $\frac{1}{2}$ is a maximum value for its average in the present problem. Some idea of the angular region over which R will be near to this maximum value can be obtained from an estimate of V_c . V_c is a slowly varying function of $\cos \theta$ and attains its maximum value at $\cos \theta = 0$. Fortunately we can estimate its value V_c^0 at $\cos \theta = 0$, without having to introduce V_L explicitly. Whereas, in an explicit calculation based on the lattice potential V_L of copper, perturbation theory would break down completely, our present method of relating V_c to other physical quantities should be satisfactory for the purpose of obtaining a numerical estimate. A similar formal use of perturbation theory has been made by Abelès (1953), Jongenburger (1953), Fumi (1955) in calculating the electrical resistivity and the energy of a vacancy in a monovalent metal which constitutes about as strong a perturbation as the one that gives rise to V_c . In the vacancy case the deviations from the exact solution were less than 30%.

V_c^0 is the sum of two contributions, namely

$$(24a) \quad V_c^{(1)} = - \int_{\text{cell}} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) V_L(\mathbf{r}) d\tau$$

and

$$(24b) \quad V_c^{(2)} = \int_{\text{cell}} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) V_L(\mathbf{r} + \mathbf{b}) d\tau.$$

$V_c^{(1)}$ can be evaluated by multiplying the Schrödinger equation

$$(25) \quad + \frac{\hbar^2}{2m} \nabla^2 \psi_{\mathbf{k}} + (\epsilon - V) \psi_{\mathbf{k}} = 0$$

by $\psi_{\mathbf{k}'}^*$ and integrating over one cell. This gives

$$(26) \quad V_c^{(1)} = +\epsilon_{\mathbf{k}'} - \epsilon = + \frac{\hbar^2 k_F^2}{2} \left(\frac{1}{m} - \frac{1}{m^*} \right) = \zeta \left(\frac{m^*}{m} - 1 \right)$$

where $\epsilon_{\mathbf{k}'} = \hbar^2 k_F^2 / 2m$ is the kinetic energy of an electron at the Fermi surface and $\zeta = \hbar^2 k_F^2 / 2m^*$ is the Fermi energy. $V_c^{(2)}$ can be estimated as follows: The main contributions to this integral come from the corners of the

Wigner-Seitz polyhedron near which $u_{\mathbf{k}}$ is a slowly varying function of \mathbf{r} only. A suitable average value $\overline{u_{\mathbf{k}}}$ may therefore be taken outside the integral. This gives

$$(27) \quad V_c^{(2)} = \overline{u_{\mathbf{k}}^*} \overline{u_{\mathbf{k}}} \int_{\text{cell}} V_L(\mathbf{r}) d\tau.$$

The integral in Eq. (27) appears also in a treatment of an interstitial atom by the method developed by Friedel (1954) and is related to the ion charge that has to be screened by the conduction electrons. If this charge is Z positive elementary charges we find, following Friedel's arguments,

$$(28) \quad V_c^{(2)} = \overline{u_{\mathbf{k}}^*} \overline{u_{\mathbf{k}}} Z \frac{1}{2} \zeta \Omega;$$

for monovalent metals we have $Z = 1$ whereas within the approximations used by Seeger (1956) $Z = 0.54$ for nickel. Within the accuracy of the present estimates it suffices to put

$$(29) \quad \overline{u_{\mathbf{k}}^*} \overline{u_{\mathbf{k}}} = 1/\Omega.$$

From the data given by Fuchs (1936) we have calculated that for the ground state wave-function in the conduction band of copper Eq. (29) holds within an accuracy of 1.5%. Somewhat larger deviations will presumably occur for wave-functions at the Fermi surface. We shall, however, not go into the details.

The result of our discussion is the estimate

$$(30) \quad V_c^0 = \zeta \left(\frac{m^*}{m} - \frac{1}{3} \right).$$

Since for Cu $m^*/m = 1.45$, for Ag $m^*/m = 1$, for Ni $m^*/m = 2$ to 3, V_c^0 is of the order of the Fermi energy and therefore rather large. If we replace V_c by V_c^0 and $\sin \alpha$ by α we can rewrite Eq. (23) as

$$(31) \quad R = \frac{1}{8} \left(\frac{m^*}{m} - \frac{1}{3} \right)^2 \frac{\Omega k_F^3}{(c k_F)^3} \frac{1}{\cos^2 \theta} = \frac{1}{8} \left(\frac{m^*}{m} - \frac{1}{3} \right)^2 \frac{3\sqrt{3}}{4} \frac{1}{\cos^2 \theta}.$$

The angle θ_0 for which $R = \frac{1}{2}$ is to the present approximation given by

$$(32) \quad \cos^2 \theta_0 = \frac{\sqrt{3}\sqrt{3}}{4} \left(\frac{m^*}{m} - \frac{1}{3} \right),$$

which for Cu gives $\cos \theta_0 = 0.8$. We conclude from this that up to a rather large value of $\cos \theta$ the reflection coefficient is relatively large, say of the order $\frac{1}{2}$ to $\frac{1}{3}$, and then decreases to a smaller value for $\theta = 0$, which may be of the order $1/10$ or smaller. Since effective masses m^* considerably smaller than the free electron mass are unlikely in the metals we are interested in, the variation of the reflection coefficient should be very similar for all metals for which a free-electron treatment is applicable.

3.4. The Electrical Resistivity of Extended Dislocations

The problem of practical interest in connection with the electron scattering by stacking-faults is the calculation of the electrical resistivity of extended dislocations. In some cases, e.g., for the calculation of the high temperature

resistivity of an extended dislocation in a metal like copper, it is presumably justified to consider the stacking-faults to be infinitely broad and to forget about the partial dislocation bounding them. If we assume one extended dislocation per unit area and take the width of its stacking-fault ribbon to be λa (a = length of elementary cube) the resistivity (measured perpendicular to the stacking-fault) is given by

$$(33) \quad \Delta\rho = \frac{9\pi\hbar\lambda a}{e^2 k_F^2} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} R(\theta, \phi) \cos^3 \theta \sin \theta d\theta d\phi.$$

Our discussion has shown that we shall obtain an upper limit to $\Delta\rho$ by putting $R \equiv \frac{1}{2}$. A result which might, at least approximately, be taken as a lower limit can be obtained by putting $R = \frac{1}{2} \sin^2 \theta$, since the actual reflection coefficient is probably always larger than that given by this expression.

For a monovalent face-centered cubic metal $a^3 k_F^3 = 12\pi^2$, and our estimate becomes therefore

$$\Delta\rho = \lambda \cdot \frac{\hbar a^3}{e^2} \cdot \omega$$

where ω lies between 0.925 and 0.3. This result (with a more conservative estimate of the lower limit) has already been given elsewhere (Seeger and Stehle 1956).

We shall base our comparison between experiment and theory on the data given in Table I. According to Stehle and Seeger the average volume increase of edge and screw dislocations in Cu is 1.5 atomic volumes for a dislocation line of length $b = a/\sqrt{2}$. In order to obtain the ratio between the additional electrical resistivity and the per cent increase in volume due to extended dislocations, we have to allow for the fact that only one-third of the stacking-faults contribute to the dislocation scattering. We obtain for that ratio

$$\frac{\frac{1}{3}\lambda\omega \cdot \hbar a^3 / e^2}{1.5} \cdot \frac{4b}{a^3} = 0.9 \cdot \lambda \cdot \omega \mu\Omega\text{-cm.}/\% \text{ increase in volume.}$$

Since the experimental value is about $2.5 \mu\Omega\text{-cm.}/\%$ increase in volume and λ should be about 6 in Cu, we obtain $\omega \approx 0.45$, which corresponds to an average reflection coefficient $R = \frac{1}{4}$. This compares quite favorably with the theoretical estimates. Similarly, good agreement is obtained for nickel. Here λ should be about the same, R should be somewhat smaller, but not very much so, and the volume increase due to an extended dislocation should be slightly larger than in copper. The main difference between Cu and Ni comes from the fact that the effective number of conduction electrons per atoms is 0.27 in nickel as compared with 1 in copper; this increases the resistivity of a stacking-fault by a factor of about four, which is just the right amount to account for the observations.

So far we have been discussing the increase of resistivity due to extended dislocations as measured at "high temperatures", since the experimental data were obtained at room temperature, where the dislocation resistivity is very small compared with the thermal resistivity. Both the experimental and the theoretical data in the low temperature range (i.e., liquid helium range) are

far less complete. We content ourselves therefore with a few remarks on the theoretical problems arising in this temperature range.

Inserting the relaxation time Eq. (22) into the low temperature formulae (10) and (10b) gives no resistivity increase. The reason for this is that in the approximation we have used (allowing for diffraction scattering only) there are always directions in \mathbf{k} -space with an infinite contribution to the conductivity. This does of course not mean that stacking-faults do not contribute to the low temperature resistivity of extended dislocations. The "short circuiting in \mathbf{k} -space" is in reality prohibited in two ways. The potential due to the overlap of ions and the incomplete shielding of the ion-core which was discussed in §2 scatters electrons at nearly all directions in \mathbf{k} -space. The same holds for the partial dislocations on both sides of the stacking-fault ribbon. Although the scattering by these mechanisms is small compared with the diffraction effect, it is essential in giving a finite contribution by the latter.

The complications just discussed give rise to deviations from Matthiessen's rule which are presumably somewhat larger than those due to unextended dislocations. For unextended dislocations the ratio of the resistivities at low and at high temperatures is of the order 2/3 (Seeger and Stehle 1956). A corresponding calculation for extended dislocations is in progress at Stuttgart; we shall therefore postpone the discussion of experimental results pertaining to this problem.

4. DISCUSSION

In §2 we have stressed the difficulties in the theory of electron scattering by stacking-faults and have stated that owing to these difficulties no satisfactory treatment is available as yet. The theory given in this paper, although giving a very useful qualitative picture, cannot be regarded as satisfactory because of the use of perturbation theory. In spite of this shortcoming it is believed that the conclusions drawn in this paper are correct for the following reasons. The method used in §3 shows that a perturbation of a stacking-fault type scatters the majority of the conduction electrons and not only those near a Brillouin zone boundary. This holds even if the perturbation is so small that perturbation theory does apply. It was possible to estimate the absolute magnitude of the scattering by relating it to known physical quantities. Although this procedure is still within the framework of perturbation theory it is known to give quite good results in similar cases. It is therefore not surprising that reasonable agreement between theory and experiment was found. The experimental value for the reflection coefficient averaged over all directions is $\frac{1}{4}$, which is much larger than the value which other authors have obtained by wave-matching methods as discussed in §2.

We are inclined to ascribe the discrepancy between the method used in this paper and the function-matching methods discussed in §2 to the incompleteness of the matching that has been done so far. The function-matching method, if carried through completely, must give the right results and should therefore produce agreement with experiment. In view of the importance

of the present problem from the experimental point of view it is highly desirable that a complete function-matching solution should be given in the near future.

We conclude with a few remarks on the experimental evidence that may be obtained from metals with few or no stacking-faults in them. The evidence on aluminum, a face-centered cubic metal with narrow stacking-faults, is rather meager but seems to be in line with the present discussion (Seeger and Stehle 1956). Recently some results have been published on the change in electrical resistivity of sodium-wires pulled 10% at liquid nitrogen temperature (Bradshaw and Pearson 1956). Sodium does not have stacking-faults; therefore the theory for unextended dislocations should apply without substantial modification. This means that the increase in resistivity should be at least 40 times smaller than that of copper cold-worked under corresponding conditions. Since the resistivity increase in moderately cold-worked copper is a small effect, it may well be below detectability in sodium. This seems to be the case in the measurements by Bradshaw and Pearson, since they report no increased resistivity in their experiments.* Therefore our picture of the dislocation resistivity seems to account for this piece of information too.

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DISCUSSION OF SEEGER'S PAPER

Ziman: I shall give a few more details about the work of Tweedale,† who estimates a much smaller value for the reflection coefficient.

The argument comes from using a modified Wigner-Seitz model—that of augmented plane waves. The approximation of plane waves is quite good in

*Point defects probably anneal out rapidly at the temperature of measuring.

†Cf. discussion of Klemens's paper.

the regions between the ion cores, and the non-planar element in the wave functions is estimated to be less than 10% of the whole. When a stacking fault is introduced, the functions have to be matched on either side of the boundary. The orbitals within the ionic spheres are not altered, and the boundary lies largely within the plane-wave region. The reflection coefficient should be proportional to the fourth power of the non-planar element, giving an estimate of 10^{-4} or 10^{-5} . As I said earlier, the model is consistent with the observed energy, though I don't want to stress this too much.

As for Dr. Seeger's much larger estimate, I am not too happy about his use of perturbation theory when the perturbation is not small.

Friedel: Were all the states up to the Fermi level considered, or just those at the bottom of the band?

Ziman: We guess that the non-planar component is not more than 10% anywhere; but we haven't done a detailed calculation to check this at the Fermi level, where of course one would expect the largest deviation.

Pines: I am unhappy about another feature of Dr. Seeger's calculation—his neglect of the redistribution of the electrons when calculating the reflection coefficient. Electrons seem to be very clever at distributing themselves in any configuration of ions so as to reduce resistance; for example, the electrical resistance in liquids is of the same order as that in solids, though the liquid is far more disordered.

Seeger: The assumption of the two half-crystals having been rigidly displaced with respect to each other is equivalent to the assumption that the shielding of the ion-core charge by the conduction electrons is completed within each atomic cell. This is thought to be a reasonable approximation in treating the diffraction effect due to stacking faults, just for the very reason that conduction electrons are quite good in screening.

I do not think there is a straightforward way of comparing the electron scattering in a liquid metal with that by a stacking fault. The scattering in a liquid metal is mainly due to the somewhat irregular arrangement of atoms in a liquid, whereas in the stacking fault we get a strong scattering due to the diffraction effect discussed in my paper even if the atoms are on their "ideal" sites. This scattering is of the same nature as the Laue-Bragg reflection by ideal crystals.

Aigrain: I don't think that the reflection coefficient can possibly be as great as 0.4. The stacking fault is equivalent to two very closely spaced twin planes, and there will be destructive interference between the two sources of scattering.

Seeger: I am not sure whether the scattering by a twin boundary and by a stacking fault are as simply related as Professor Aigrain suggests. After all, the main scattering by a stacking fault arises from diffraction by the lattice behind the stacking-fault plane. Furthermore, the experiments on twin boundaries in silicon should not be compared with the data on copper, since the conduction electrons in silicon behave much more like free electrons than the electrons at the Fermi surface of copper.

ON THE STATISTICAL MECHANICS OF IRREVERSIBLE PROCESSES¹

BY I. PRIGOGINE²

1. INTRODUCTION

In his classical paper on thermal conductivity of solids, Peierls (1929) assumed that the approach of the distribution function $\rho(E_1, E_2, \dots, t)$ of the energies of the normal modes toward equilibrium may be described by a Fokker-Planck diffusion equation. Let us write it in the general form

$$(1.1) \quad \frac{\partial \rho(E_1 \dots E_i \dots; t)}{\partial t} = O\rho(E_1 \dots E_i \dots; t).$$

Here the operator O has to be self-adjoint in order to obtain a spectrum of real relaxation times. To obtain the explicit form of O it is only necessary, once the assumption of a Fokker-Planck scheme is made, to calculate the averages

$$(1.2) \quad \overline{\Delta E_k}, \quad \overline{\Delta E_k \Delta E_{k'}}.$$

This Peierls did by a second-order perturbation technique. Once the explicit form of (1.1) is established it is easy to derive the equation of change for $\overline{E_k}$, which was found to be of the form

$$(1.3) \quad \frac{d\overline{E_k}}{dt} = \sum_{k', k''} C_{kk', k''} (\omega_k \overline{E_{k'} E_{k''}} + \omega_{k'} \overline{E_k E_{k''}} + \omega_{k''} \overline{E_k E_{k'}}).$$

Here $C_{kk', k''}$ is symmetric in the three indexes k, k', k'' . If finally one assumes the factorization of the distribution functions at every time

$$(1.4) \quad \rho(E_1 \dots E_i \dots; t) = \prod_k \rho_k(E_k, t),$$

one may write (1.3) in the usual form

$$(1.5) \quad \frac{d\overline{E_k}}{dt} = \sum_{k', k''} C_{kk', k''} \omega_k (\overline{E_{k'}} \overline{E_{k''}} + \overline{E_{k'}} \overline{E_k} + \overline{E_{k''}} \overline{E_k}).$$

The occurrence of the products in the right-hand side of (1.5) corresponds to a binary collision mechanism between normal modes (or phonons). Such a procedure is quite characteristic of the whole technique of irreversible processes.

In the case of electrons in metals one generally writes down directly the Boltzmann equation (1.5) which then corresponds, for example, to "collisions" between electrons and ions. However, Uhlenbeck (1955), Siegert (1949), and Kac (1954) have called attention to the fact that here also one may start with a linear equation similar to (1.1) which describes a Markoffian process, and then derive the Boltzmann equation as a moment equation. However in this case O is no longer a differential but an integrodifferential operator. It is hereafter called the master equation.

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In every case the theory of irreversible processes is based on a mixture of mechanical and probabilistic concepts. One might briefly say that it is based on random processes in which the parameters are calculated from mechanical considerations (for example, by perturbation principles). Such a procedure has clearly to be justified and its limitations discussed. If it is true that we may at some initial time assume rather arbitrarily the form of the distribution function (classical or quantal), this is no longer true at a later time and we have to compare the assumed random processes to the exact evolution as predicted by mechanics.

These problems have been largely clarified in the past years (Klein and Prigogine 1953; Van Hove 1955; Brout and Prigogine 1956 *a, b, c*; Brout 1956; Van Hove 1956) and the results show what may be called a beginning of a statistical mechanics of irreversible processes of a generality comparable to equilibrium statistical mechanics. We shall not try to go into details of calculations but show the main ingredients which go into the present theory.

2. MECHANICAL PROCESSES

We shall be concerned mainly with classical mechanisms (Brout and Prigogine 1956 *a, b, c*) because it is in this case where the most detailed results have been obtained so far. The evolution of the distribution function in phase space $\rho(q_1 \dots q_N, p_1 \dots p_N; t)$ then satisfies the Liouville equation

$$(2.1) \quad \frac{\partial \rho}{\partial t} + [H, \rho] = 0.$$

The $[H, \rho]$ is the well-known Poisson bracket of the Hamiltonian H with ρ :

$$(2.2) \quad [H, \rho] = \sum_{i=1}^N \left(\frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right).$$

One of our basic problems is clearly to show the relation of the reversible mechanical process (2.1) to the master equation (1.1) and therefore to the "Boltzmann" equation (1.5).

Let us write (2.1) in the form

$$(2.3) \quad i \frac{\partial \rho}{\partial t} = L\rho.$$

It may now be easily verified that L is here a self-adjoint (or Hermitian) operator, with eigenvalues λ_k corresponding to the eigenfunctions ϕ_k :

$$(2.4) \quad L\phi_k = \lambda_k \phi_k.$$

The λ_k are therefore real and we have also the other usual properties so familiar from quantum mechanics. For example, we may expand ρ in terms of the ϕ_k :

$$(2.5) \quad \rho(p, q; t) = \sum_k C_k \exp(-i\lambda_k t) \phi_k(p, q).$$

Let us stress the fact that the time appears only in the imaginary exponential, which is clearly related to the reversibility of the mechanical equations of motion.

Now the Liouville operator L takes an especially simple form if it is possible

to introduce as canonical variables the angle-action variables $\alpha_1 \dots \alpha_N$, $J_1 \dots J_N$ such that the Hamiltonian takes the form

$$(2.6) \quad H = \sum H_i(J_i).$$

The motion may here be characterized by the frequencies

$$(2.7) \quad \nu_i = \partial H / \partial J_i$$

and all physical quantities are periodic functions of the α . In the case of a harmonic oscillation the transition from p, q to J, α is similar to the transformation from rectangular to polar coordinates. Also in the case of free translation one has

$$J \sim p$$

and

$$\alpha \sim r.$$

With these variables the Liouville operator takes the form

$$(2.8) \quad L = -i \sum \nu_k \frac{\partial}{\partial \alpha_k}.$$

Therefore the eigenfunctions are of the form

$$(2.9) \quad \prod_k \exp(in_k \alpha_k) \quad (n_1, n_2 \dots \text{integers})$$

and the eigenvalues

$$(2.10) \quad \lambda_{\{n\}} = \sum_k n_k \nu_k$$

(where $\{n\}$ is always an abbreviation for the set of integers n_1, n_2, \dots, n_N).

The spectral decomposition (2.5) therefore takes the more explicit form

$$(2.11) \quad \rho(J_1 \dots J_N, \alpha_1 \dots \alpha_N; t) \\ = \sum_{\{n\}} \rho_{\{n\}}(J_1 \dots J_N; 0) \exp[i \sum n_k (\alpha_k - \nu_k t)]$$

with

$$(2.12) \quad \rho_{\{n\}}(J_1 \dots J_N; 0) \\ \sim \int \dots \int \rho(J_1 \dots J_N, \alpha_1 \dots \alpha_N; 0) \exp[-i \sum n_k \alpha_k] d\alpha_1 \dots d\alpha_N.$$

Of special importance will be the coefficient

$$(2.13) \quad \rho_{\{0\}} \sim \int \rho d\alpha_1 \dots d\alpha_N.$$

It is simply the phase average of ρ (or the average over the whole space in the case of translation).

Let us now consider in more detail the kind of Hamiltonians in which we shall be interested.

3. WEAKLY COUPLED SYSTEMS

A well-known difficulty in statistical mechanics of irreversible processes is that the approach to complete thermodynamic equilibrium is possible only for nonseparable systems. For example in the case of (2.6) every action J_k is a constant, while according to statistical equilibrium theory the distribution function should depend only on the total energy (and eventually also on the

total momentum and angular momentum). The simplest situation in which approach toward thermodynamic equilibrium is possible is therefore what may be called a weakly coupled system in which the Hamiltonian is of the form

$$(3.1) \quad H = H_0 + \lambda V$$

where H_0 is separable in the sense of (2.6) while the perturbation λV (λ is a coupling constant) mixes all the invariants of H_0 . Weakly coupled systems means then either that in all possible configurations

$$(3.2) \quad |V| \ll |H_0|$$

or that at least (3.2) is valid in a time averaged sense. The first case corresponds, for example, to weak electron lattice-vibration coupling, or to "soft" long range interactions. The second would correspond to short range forces in a dilute gas.

We shall treat in detail the simplest case in which (3.2) is satisfied. We may then use a straightforward method of expansion in powers of λ (or better, as we shall see later, of $\lambda^2 t$), while in the second case it is necessary to introduce some other expansion parameters (for example, the concentration for dilute gases).

The decomposition (3.1) means that we may distinguish two time scales in time evolution of the system: a short time scale related to H_0 and a long one due to λV .

Let us consider first the evolution of a system in the short time scale.

4. EFFECT OF H_0

In spite of the over-all nonergodicity of a system in which the Hamiltonian reduces to the separable part H_0 , there exist local irreversible processes which bring the system as near as possible to the state of final thermodynamic equilibrium. This arises through the mixing of the initial conditions. Suppose that the initial mechanical variables are only known in probability. Then as time goes on any mechanical variables will depend on more and more random variables, which are the initial data. Therefore the existence of asymptotic laws largely independent of the initial distribution is to be expected. The situation is very similar to that of the classical central limit theorem in the theory of probabilities. The example of crystal lattices has been analyzed in detail along these lines (Klein and Prigogine 1953; Prigogine and Bingen 1955).

Let us only quote a result in the simplest case, which corresponds to a one-dimensional lattice with nearest neighbor interactions. Let us call y_{2n} the velocity of the n th particle, y_{2n+1} the distance (minus the equilibrium distance) between the n th and the $(n+1)$ th particle. Both y_{2n} and y_{2n+1} are made dimensionless by division by suitable quantities. It may then be easily shown that if we consider a so-called *local distribution function* $\rho(y_k \dots y_{k+n}, t)$ obtained by integration of $\rho(y_1 \dots y_N, t)$ over all variables except $y_k \dots y_{k+n}$, such distribution functions tend asymptotically to the Gaussian form as t tends to infinity:

$$(4.1) \quad \rho(y_k \dots y_{k+n}, t) \rightarrow \exp \left[- \sum_{i,j=k}^{k+n} a_{ij} y_i y_j \right].$$

This asymptotic distribution differs from the equilibrium one only by the fact that the correlations

$$(4.2) \quad \overline{I_n} = \overline{y_k y_{k+n}}$$

do not vanish. The magnitude of the $\overline{I_n}$ is related to a nonuniformity in the distribution of the energies of normal modes. Indeed one can show that

$$(4.3) \quad E_\phi = \sum_n I_n \exp(i\phi n).$$

Therefore the correlation I_n may only vanish if one has already equipartition of energy. Irregular inhomogeneities are also destroyed during this short time scale (while macroscopic gradients are not, because of the time necessary for the energy to flow over such regions).

Let us now consider the effect of the perturbation V .

5. EFFECT OF THE PERTURBATION V —GENERAL CONSIDERATIONS

The method we shall use is to start from (2.4) but to consider now the Fourier coefficients $\rho_{(n)}$ as time dependent. We therefore follow closely the usual method of variation of constants. Before writing down the equations for the $\rho_{(n)}$ we have to consider more closely the nature of the systems in which we may hope to find an irreversible approach to equilibrium. Clearly because of Poincaré's recurrence theorem we need a system with a large number of degrees of freedom and with time small with respect to Poincaré's recurrence time. Also we have to express that V couples all subsystems. This in turn is related to conditions first stated by Poincaré (1892) when he studied the destruction of analytical invariants by a perturbation. These two features, the large number of degrees of freedom and the destruction of the previous invariants, may be expressed in an elegant form as pointed out by Van Hove (1955) in the quantum case. This is the condition of diagonal singularity. It seems interesting to give an example.

For interacting gas molecules the perturbation potential may be written in the form

$$(5.1) \quad V = \sum_{i,j} V(r_{ij}),$$

which ensures that every molecule is coupled to every other. Let us now develop V as a Fourier expansion in the angle variables (or the coordinates)

$$(5.2) \quad V = \sum_{\{k\}} V_{\{k\}} \exp \left[i \sum_i \mathbf{k}_i \cdot \mathbf{r}_i \right].$$

With (5.1) the only $\{k\}$ that enters into (5.2) is of the form $(0 \dots k, 0 \dots k_m, 0 \dots 0)$ with

$$(5.3) \quad \mathbf{k}_i + \mathbf{k}_m = 0.$$

This is a quite general situation because of the fact that V is the sum of contributions due only to a few molecules. The Fourier coefficients $V_{\{k\}}$ are generally simple functions of the wave numbers. We may also take

$$(5.4) \quad V_{\{0\}} = 0$$

because $V_{[0]}$ may be added to H_0 . Let us now consider the sum

$$(5.5) \quad \sum_{\{k'\}} V_{[k-k']} V_{[k''-k']}$$

or more explicitly

$$(5.6) \quad \sum_{k_1'' \dots k_N''} V_{k_1-k_1'', k_2-k_2'', \dots, k_N-k_N''} V_{k_1''-k_1', k_2''-k_2', \dots, k_N''-k_N'}.$$

The number of terms which contribute effectively to such sums depends on the values of $\{k\}$ and $\{k'\}$ which are given. If we consider the "diagonal" terms

$$(5.7) \quad \{k\} = \{k'\}$$

we obtain nonvanishing contributions to (5.6) for $k_1'' = k_1, k_2'' = k_2, \dots$ except for two arbitrary indices. Therefore the number of sums in (5.6) is

$$\frac{1}{2}N(N-1).$$

On the contrary if we consider nondiagonal terms

$$\{k\} \neq \{k'\},$$

it may be easily verified that each of such nondiagonal terms gives a contribution in which the number of terms is smaller at least by a factor of $1/N$. Therefore in the limit of an infinite system the diagonal terms present a singularity due to the infinite number of intermediate states over which the summation may be performed.

Let us also make more precise what is called a weakly coupled system. This means that in the final analysis only the smallest power of the coupling parameter λ is retained. At the same time however we wish to study the evolution for long times. For weakly coupled systems there exists no contribution of the form λt (this may be verified from the usual second-order perturbation technique) but only terms of the form $\lambda^2 t$ (and perhaps $\lambda^n t$, $n > 2$). The method used here is to retain only powers of $\lambda^2 t$ and to neglect contributions of the form $\lambda^n t$ with $n > 2$ (or powers of such contributions).

Finally we may stress here the similarity between field theory problems (e.g. self-energy) and the problem of the approach to equilibrium (Van Hove 1955). In both cases we deal with persistent perturbations quite different from the usual scattering problems.

6. EFFECT OF V -PERTURBATION CALCULATION

After the preliminary considerations of §5 we may briefly summarize the actual perturbation technique. We start with the expression (2.4). Let us consider the Fourier coefficients $\rho_{[n]}$ to be functions of time. To the perturbation λV corresponds the perturbation of the Liouville operator

$$(6.1) \quad \lambda \delta L = \lambda i \sum_j \left(-\frac{\partial V}{\partial \alpha_j} \frac{\partial}{\partial J_j} + \frac{\partial V}{\partial J_j} \frac{\partial}{\partial \alpha_j} \right).$$

One has an infinite set of simultaneous equations for the $\rho_{[n]}$ which are solved by iteration. Let us write down the first terms of the expansion obtained in this way,

$$\begin{aligned}
 (6.2) \quad \rho_{\{n\}}(J_1 \dots J_N; t) &= \rho_{\{n\}}(J_1 \dots J_N; 0) \\
 &+ \lambda \sum_{\{n'\}} \int_0^t dt_1 \langle \{n\} | \exp[-i \sum n_i \nu_i t] \delta L \exp[i \sum n'_i \nu_i t] | \{n'\} \rangle \rho_{\{n'\}}(0) \\
 &+ \lambda^2 \sum_{\{n_1\}} \sum_{\{n_2\}} \int_0^t dt_2 \int_0^{t_2} dt_1 \langle \{n\} | \exp[-i \sum n_i \nu_i t] \delta L \exp[i \sum n_{2,i} \nu_i t_2] | \{n_2\} \rangle \\
 &\times \langle \{n_2\} | \exp[-i \sum n_{2,i} \nu_i t_1] \delta L \exp[i \sum n_{2,i} \nu_i t_1] | \{n_1\} \rangle \rho_{\{n_1\}}(0) \\
 &+ \dots
 \end{aligned}$$

with the definition of the matrix element

$$(6.3) \quad \langle \{n\} | A | \{n'\} \rangle = \int \dots \int d\alpha_1 \dots d\alpha_N \exp[-i \sum n_i \alpha_i] A \exp[i \sum n'_i \alpha_i].$$

The structure of the series is obvious. We have now to extract powers of $\lambda^2 t$. This becomes possible for sufficiently large times (in the short time scale) in the limit of $N \rightarrow \infty$ using the condition of diagonal singularity and the occurrence of resonance conditions.

Proceeding in this way we obtain finally for $\rho_{\{n\}}$ the diagonal set of equations

$$(6.4) \quad \frac{\partial \rho_{\{n\}}}{\partial t} = \lambda^2 \Omega_{\{n\}} \rho_{\{n\}}$$

where $\Omega_{\{n\}}$ is a differential operator. For $\{n\} = 0$ it has the simpler form

$$(6.5) \quad \frac{\partial \rho_{\{0\}}}{\partial t} = \sum_{\{k\}}' \sum_{l, l'} k_l k_{l'} \frac{\partial}{\partial J_l} (V_{\{k\}})^2 \frac{\partial}{\partial J_{l'}} \rho_{\{0\}}.$$

The right-hand side is a self-adjoint operator and (6.5) represents a Fokker-Planck equation. In the case of the usual interaction between normal modes in a solid, Peierls's equation (1.1) is recovered.

However the differential operator $\Omega_{\{n\}}$ for $\{n\} \neq \{0\}$ has not this simple form and does not reduce to a Markoffian process.

We see therefore that it is only one of the Fourier components of the distribution function corresponding to an average over all the angles (or over the positions) that presents an irreversible behavior.

This gives a precise meaning to the coarse graining of a distribution function which has been so often described in qualitative terms.

From (6.5) follows directly an H -theorem which is defined in terms of $\rho_{\{0\}}$. Also from the diagonal form of the equation (6.4) it follows that if the distribution is initially phase independent it remains so. Moreover if the distribution function is initially factorized in the sense of (1.4) it remains so.

In the case when it is only the time average of the perturbation which is small the final equation for $\rho_{\{0\}}$ is also a Markoffian equation but of the integro-differential Boltzmann type (Brout 1956). This is also the case for weakly coupled quantum systems (Van Hove 1956). We see that there is a close connection between the special type of Markoffian processes and the form of the Hamiltonian.

Finally let us consider the effect of a gradient extending over macroscopic regions.

7. MACROSCOPIC GRADIENTS

If there exists no macroscopic gradient, H_0 will homogenize the system in the short time scale and we may describe its evolution in terms of $\rho_{(0)}$ alone. This is no longer the case when we have a macroscopic gradient (i.e. a gradient in temperature $\partial T/\partial x$). There we have to use other $\rho_{(n)}$ apart from $\rho_{(0)}$ for the description of a system. Now (6.4) shows that $\rho_{(n)}(t)$ is a function of $\rho_{(n)}(0)$ alone. Thus $\partial \rho_{(n)}/\partial t$ contains the product $\lambda^2 \rho_{(n)}(0)$ which is of the order $\lambda^2 \partial T/\partial x$. If both the gradient and the coupling parameter are small this is a quantity of the second order.

Let us write down schematically the time variation of ρ :

$$(7.1) \quad \frac{\partial \rho}{\partial t} = \frac{\partial \rho_{(0)}}{\partial t} + \sum_{|n|} \frac{\partial \rho_{(n)}}{\partial t} \exp[i \sum n_i (\alpha_i - \nu_i t)] + \left(\frac{\partial \rho}{\partial t} \right)_{\text{harm}}$$

where $(\lambda \rho/\partial t)_{\text{harm}}$ is the time dependence due to the oscillating exponents in (2.11). The first term in (7.1) is proportional to λ^2 ; the last is the variation of ρ due to harmonic forces, which is of the order of the temperature gradient. The second term is of the order $(\partial T/\partial x)\lambda^2$ and is negligible with respect to the two others. In this approximation the evolution of the distribution function may be described as the sum of two additive parts: a Markoffian process described by $\partial \rho_{(0)}/\partial t$ and a unitary flow process $(\partial \rho/\partial t)_{\text{harm}}$. This corresponds exactly to the usual Boltzmann transformation where the decay due to collisions is added to the streaming term. However we see that for large gradients this would require solutions of all the equations (6.4). Using the initial preparation of the system by H_0 and the Boltzmann equation (1.5) one might by small gradients give in simple cases the explicit value of the thermal conductivity by writing down the change of the second moments \bar{I}_k obtained by (4.2). We shall however not go into more details, but refer to our original publication (Brout and Prigogine 1956b).

8. CONCLUSIONS

Concluding we may say that there exists now a rather complete description of an equation of irreversible processes starting from first principles. This has proved to be of rather general significance. However the exact value of such a conception has to be judged in the future from the number of new applications it will be able to develop.

I wish to state that the main results described here have been obtained in collaboration with Dr. Robert Brout.

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DISCUSSION OF PRIGOGINE'S PAPER

Prigogine (in answer to a question by Fröhlich): In a gas at least we are justified in neglecting terms except those in λ^2 , since the interaction is weak.

Fröhlich: A gas may be all right, but what about electrons in metals?

Prigogine: This we have not considered. It is certainly all right for one solid-state problem, that of the insulator whose normal vibrations are coupled by anharmonic forces, since here we can consider the interactions to be sufficiently small.

Mott: Will your treatment lead to any modification of the present theory of thermal conductivity?

Prigogine: In principle, yes. As we have seen, with H_0 alone the correlations $\overline{I_k} = \overline{y_n y_{n+k}}$ are invariant. $\overline{I_1}$ can easily be shown to be the energy flow, and thus without anharmonic terms the heat flow will be conserved, so that there is no thermal resistance.

When there is a finite thermal resistance we have to consider the steady state in which $\overline{I_1}$ is maintained by a macroscopic gradient. The equation $d\overline{I_1}/dt = 0$ when expanded (cf. 7.1) is to the first order equivalent to the ordinary heat flow equation, though as in Peierls's treatment the coefficient giving the relaxation time appears as a very complicated Fourier transform that is at present useless for calculation. There are however further terms which will become important for *large* thermal gradients, and it is here that we may expect an extension to the present theory.

de Boer: The theory also may have useful applications to the theory of gases. The usual treatment of conductivity and viscosity in gases uses the Boltzmann equation, which is essentially dependent on two-body molecular collisions only. Now the master equation contains no such limitation, and enables us to consider many-body collisions.

In principle this also should be applicable to metals.

Sondheimer: What is the difference between this and the theory of Born and Green?

de Boer: Born and Green did not introduce the irreversibility explicitly, but sought to derive everything purely from the Liouville equation.

Sondheimer: At what point does time irreversibility come into the present theory?

Prigogine: In the resonance equation, I think.

MacDonald: The recent conference in Brussels organized by Professor Prigogine considered at some length the foundations and limitations of the Boltzmann equation—particularly in relation to the problems of gases. I sometimes feel some surprise that little attention seems to be paid to the problem of the validity of the Boltzmann equation as applied to electrons in a solid. Thus in a classic textbook such as Wilson's the establishment of the Boltzmann equation seems to be dismissed very briefly. I'm also rather worried at times about the validity of a Boltzmann equation to describe the "phonons" in the case of thermal conduction in an insulator.

Prigogine: Theories used in the past have been at least partly intuitive and not based on rigor, although some of them, like Peierls's, are almost un-

doubtedly correct. But for large gradients Boltzmann's equation is not true—for example in the theory of high frequency absorption—and it is here that our more deductive formalism is needed.

Seeger: What have you to say about the theory of rate processes developed by Eyring and others?

Prigogine: Here there are many other difficulties. The theory is based on the one-particle model—e.g., you consider the diffusion of one particle when all the others are kept fixed. This is obviously not a good picture and in fact the results disagree with experiment. What we need is a more collective description—in fact, a better model for a liquid.

Seeger: Eyring's theory works quite well in solids.

Prigogine: The one-particle approximation is much better in solids.

Seeger: The Eyring-Zener theory is quite successful for a vacancy or interstitial atom. But when we have a dislocation, in which irregularities are coupled together, our problem is to determine what then is meant by the activation energy and frequency factor.

Prigogine: Some progress may be possible along the lines I have described.

Bardeen: This is all a little reminiscent of the dispersion theory approach in electrical conductivity, in which we suppose we know the exact equilibrium distribution and treat the field as a perturbation; for this we require the properties including scattering but in the absence of a field.

Kubo: This is similar to the theory of damping.

May I ask Professor de Boer if it is indeed possible in this theory to treat triple collisions?

de Boer: Yes, though we are limited to two-body potentials.

MacDonald: Professor Prigogine has said there will be no thermal resistance in a linear chain if there are no terms above the third order in the potential. Has he confirmed Peierls's assertion that fourth order terms are sufficient for a finite resistance?

Prigogine: No. But I think the theory will confirm this.

ELECTRON-PHONON EQUILIBRIUM AND THE TRANSPORT PHENOMENA IN METALS AT LOW TEMPERATURES¹

BY E. H. SONDHEIMER²

In the theory of the transport phenomena in electronic conductors one is dealing with a system of two components, the electrons (carrying charge and energy, obeying Fermi statistics) and the quantized lattice waves ('phonons', which carry energy only and obey Bose statistics). The electrons and phonons scatter each other, and it is this interaction which is the main factor in determining the electrical resistance of metals. To calculate the transport magnitudes the usual procedure is to set up the Boltzmann equation for the steady-state distribution function f of the electrons in the presence of applied fields, i.e. $[\partial f / \partial t]_{\text{fields}} + [\partial f / \partial t]_{\text{coll}} = 0$, where the second term is the net rate of change in f produced by the collision mechanisms. The expression for $[\partial f / \partial t]_{\text{coll}}$ involves factors of the type

$$[1] \quad U(\mathbf{k}', \mathbf{k}) f(\mathbf{k}') \{1 - f(\mathbf{k})\} \{N(\mathbf{q}) + 1\} - U(\mathbf{k}, \mathbf{k}') f(\mathbf{k}) \{1 - f(\mathbf{k}')\} N(\mathbf{q}),$$

where $N(\mathbf{q})$ is the phonon distribution function, and where the first term, for example, corresponds to a transition of an electron from a state characterized by the wave vector \mathbf{k}' to the state \mathbf{k} , with emission of a phonon with wave vector \mathbf{q} . The expression [1] must vanish in the equilibrium state (when $f = f_0$, the Fermi function, and $N = N_0$, the Bose function), and this requirement is satisfied if the transition probability $U(\mathbf{k}, \mathbf{k}')$ satisfies the symmetry relation

$$[2] \quad U(\mathbf{k}, \mathbf{k}') = U(\mathbf{k}', \mathbf{k}),$$

which expresses the principle of microscopic reversibility. To obtain f for the steady non-equilibrium state, it is usual to put $f = f_0 + f_1$, but to assume that N has the equilibrium value N_0 , and to retain terms linear in f_1 ; we then obtain a linear integral equation to be solved for f_1 . But this procedure is really inconsistent, since the electron-phonon collisions also tend to change N , and the expression for $[\partial N / \partial t]_{\text{coll}}$ also contains factors of the form [1], and is non-zero if $f \neq f_0$ and $N = N_0$; thus the phonons cannot be in equilibrium. This difficulty is ignored in the usual theory, in which the non-equilibrium electron and phonon distributions are determined separately, the former by supposing the phonons to be in equilibrium, and the latter (when required) from a phonon Boltzmann equation in which the electrons are supposed to be in equilibrium.

In order to produce a consistent theory it is necessary to suppose that $f \neq f_0$ and $N \neq N_0$ simultaneously, and to determine f and N from two simultaneous Boltzmann equations. In setting up these equations, care

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must be taken to treat the electron-lattice interaction symmetrically, in such a way that the non-equilibrium phonon distribution function enters into the electron Boltzmann equation in the same way that the non-equilibrium electron distribution function enters into the phonon Boltzmann equation; this symmetry requirement, to which insufficient attention has sometimes been paid in the past ((16), Appendix; (3)), is needed, in conjunction with the symmetry property [2], to ensure the validity of the Kelvin relations among the thermoelectric effects ((23); see also (29)).

Particular aspects of the problem have been considered at various times in the past, and the subject has again come into prominence recently in connection with the anomalous thermoelectric behavior of semiconductors at low temperatures (2, 5). Here, however, we consider only the influence of the lattice non-equilibrium upon the transport phenomena in metals (in the absence of magnetic fields), with particular reference to the possible bearing of the results upon the discrepancies between the experimental facts and the usual form of the theory in which the lattice is supposed to be in equilibrium.

We consider first the thermoelectric power Q . The general form of the additional term Q_θ in Q which arises from the non-equilibrium of the lattice can be derived by simple qualitative arguments ((12); see also (10)). When the phonon distribution is anisotropic, the electron-phonon interaction leads to a transfer of directed momentum to the electrons (the electrons are 'swept along by the lattice waves'), and an additional thermoelectric field is needed to prevent an electric current from flowing. By considering the equilibrium of an elementary region of the lattice, it is easy to show that

$$[3] \quad Q_\theta \sim \frac{C_v}{ne} \frac{\tau_p}{\tau_e + \tau_p},$$

where C_v is the specific heat of the lattice, n is the number of electrons per unit volume, e is the electronic charge, τ_e is an effective time of relaxation for electron-phonon scattering, while τ_p is the time of relaxation for all other phonon scattering mechanisms. It is to be noted that Q_θ is a 'first-order' quantity (i.e., is non-zero for a completely degenerate electron gas), in contrast to the result Q_e given by the usual theory, which is of the order of $C_v^{(e)}/ne$, where $C_v^{(e)}$, the specific heat of the conduction electrons, is zero for completely degenerate electrons.

The expression [3] has only rough qualitative significance. In a more exact theory a number of generalizations are necessary, the most important of which arises from the impossibility of defining τ_e uniquely at low temperatures (26); other factors to be considered include the frequency variation of τ_p , and variations in the strength of the electron-phonon interaction for lattice waves of different directions of polarization. A systematic treatment (4), based upon the usual assumptions of the Bloch theory concerning the energy spectrum of electrons and lattice vibrations and the form of the matrix elements for electron-phonon scattering (but in which the electron-phonon interaction is not restricted to longitudinal phonons), leads to approximate ex-

pressions for the 'lattice' terms in the transport coefficients which may all be expressed in terms of the integral

$$[4] \quad \mathcal{Q}_{j,n} = \int_0^{\Theta/T} \left\{ \alpha_j z + 2^{-5/3} N_a^{-4/3} \frac{T_0}{T} \frac{l}{L(z, T)} \right\}^{-1} \frac{z^n dz}{(e^z - 1)(1 - e^{-z})},$$

in which Θ is the Debye temperature, l is the free path for electron-phonon scattering at a temperature $T_0 > \Theta$, l/α_j (with $\sum_j \alpha_j = 1$) is the partial free path for scattering of electrons by lattice waves of polarization j , $L(z, T)$ is the resultant free path (frequency-dependent in general) for scattering of phonons by all causes other than conduction electrons, and N_a is the number of conduction electrons per atom.

With this notation the results obtained for the electrical resistivity ρ , the thermal conductivity κ , and the thermoelectric power Q take the form

$$[5] \quad \rho = \rho_e + \rho_\theta, \quad \kappa = \kappa_e + \kappa_\theta, \quad Q = Q_e + Q_\theta,$$

where the 'electronic' terms ρ_e , κ_e , and Q_e are the same as those obtained in the theory which assumes the lattice to be in equilibrium, and where the 'lattice' terms are given by

$$[6] \quad \rho_\theta = 4A \left(\frac{T}{\Theta} \right)^5 \sum_j \alpha_j^2 \mathcal{Q}_{j,6},$$

$$[7] \quad \kappa_\theta = \frac{3\Theta L_n}{4\pi^2 A N_a^2} \left(\frac{T}{\Theta} \right)^2 \sum_j \mathcal{Q}_{j,4},$$

$$[8] \quad Q_\theta = -\frac{k}{eN_a} \left(\frac{T}{\Theta} \right)^3 \sum_j \alpha_j \mathcal{Q}_{j,5},$$

L_n being the Lorenz number, and A being defined by the expression AT/Θ for the 'ideal' part of ρ_e at high temperatures. Equation [8] represents the required generalization of equation [3], an expression resembling [6] has previously been given by Klemens (7), while the expression [7] is identical with the usual expression for the lattice thermal conductivity of metals, derived on the supposition that the conduction electrons are in equilibrium ((26), p. 294); in the case of κ , therefore, the present theory merely confirms the usual approach (but it must be remembered that the solutions of the transport equations which lead to [5] are not exact at intermediate temperatures; the effect of the higher-order corrections is not at present known). We now discuss the predictions of equations [6]–[8] when the 'phonon' free path $L(z, T)$ has certain special forms, assumed to be characteristic for particular ranges of temperature.

'PHONON-PHONON' SCATTERING

At high temperatures ($T > \Theta$) $L(z, T)$ is limited essentially by the scattering of lattice waves by one another, arising from the anharmonic terms in the potential energy of the lattice. Denoting the corresponding free path by L_a , we have, when Θ/T is small,

$$[9] \quad \mathcal{Q}_{j,n} = \frac{2}{n-1} (2N_a^2)^{2/3} \frac{\Theta L_a}{T_0 l} \left(\frac{\Theta}{T} \right)^{n-2},$$

and we find, from [6], [7], [8] and the standard expressions for ρ_e , κ_e , and Q_e at high temperatures, that the ratios of the 'lattice' to the 'electronic' terms are given by

$$[10] \quad \frac{\rho_\theta}{\rho_e} = \frac{8}{5} (2N_a^2)^{2/3} \frac{\Theta L_a}{T_0 l} \sum_j \alpha_j^2,$$

$$[11] \quad \frac{\kappa_\theta}{\kappa_e} = \frac{3}{\pi^2} (2N_a^2)^{-1/3} \frac{\Theta L_a}{T_0 l},$$

$$[12] \quad \frac{Q_\theta}{Q_e} = \frac{1}{\pi^2} (\frac{1}{2} N_a)^{1/3} \frac{\zeta}{kT} \frac{\Theta L_a}{T_0 l},$$

where ζ is the Fermi level. The absolute values of these expressions are difficult to estimate, in view of our lack of knowledge regarding the value of L_a in metals (but κ_θ is probably not greater than a few per cent of κ_e in good metals). We note, however, that

$$[13] \quad \frac{\rho_\theta}{\rho_e} = \frac{16}{15} \pi^2 N_a^2 \sum_j \alpha_j^2 \frac{\kappa_\theta}{\kappa_e}, \quad \frac{Q_\theta}{Q_e} = \frac{1}{3} N_a \frac{\zeta}{kT} \frac{\kappa_\theta}{\kappa_e};$$

since $\sum_j \alpha_j^2 \gg \frac{1}{3}$, ρ_θ/ρ_e is therefore in monovalent metals at least $16\pi^2/45 = 3.5$ times as large as κ_θ/κ_e . Also, for normal values of ζ and N_a , $Q_\theta/Q_e \gg \kappa_\theta/\kappa_e$, so that Q_θ may be expected to be comparable in magnitude with Q_e at ordinary temperatures. Finally, since L_a is proportional to T^{-1} , while ρ_e and Q_e are proportional to T , ρ_θ is independent of T and Q_θ varies as T^{-1} . It is not known with certainty whether ρ_θ and Q_θ ever play any role in practice at high temperatures. For the monovalent metals, at any rate, the anomalies that occur at high temperatures (such as the anomalous positive sign of Q in Li, Cu, Ag, Au) do not seem to be ascribable to the effect of the lattice terms, but the decrease in $|Q|$ with increasing T which is observed, for example, in bismuth at high temperatures (21) could perhaps be explained by supposing that Q_θ gives the dominant contribution to Q in this case.

SCATTERING BY CONDUCTION ELECTRONS AND BY POINT IMPERFECTIONS

At temperatures below Θ the phonons are scattered mainly by conduction electrons and by lattice defects of various types. We shall suppose that, except at extremely low temperatures where boundary scattering becomes important (see below), the imperfections can be assumed to scatter as the fourth power of the frequency, as predicted by theory for the scattering of low-frequency waves by point defects (for a discussion of this and other types of defect scattering see Klemens (11)). We may therefore write

$$[14] \quad 1/L(z, T) = \mathcal{J} z^4 (T/\Theta)^4,$$

where \mathcal{J} is a constant, and

$$[15] \quad \mathcal{Q}_{J,n} = \int_0^{\Theta/T} \left\{ \alpha_j + p \left(\frac{T}{\Theta} \right)^3 z^3 \right\}^{-1} \frac{z^{n-1} dz}{(e^z - 1)(1 - e^{-z})}$$

where p is a constant proportional to \mathcal{J} .

Considering first the thermoelectric power, we find from [8] and [15] that

$$[16] \quad \mathcal{S}_e = -77.8 \frac{k}{eN_a} \left(\frac{T}{\Theta} \right)^3$$

at very low temperatures, when scattering by conduction electrons is dominant, and that Q_θ increases with increasing T towards the limiting value

$$[17] \quad Q_\theta = -\frac{k}{3eN_a} \sum_j \frac{\alpha_j}{p} \ln \left(1 + \frac{p}{\alpha_j} \right).$$

On the other hand, $Q_e = -x\pi^2 k^2 T / e\zeta$, where $x = \frac{1}{3}$ at very low and $x = 1$ at high temperatures. It is clear that the relative importance of Q_θ and Q_e depends critically upon the value of p ; when $p = 0$, in particular, (i.e. when phonons are supposed to be scattered by electrons only), Q_θ greatly exceeds Q_e for all temperatures above a few degrees absolute, and the values of Q obtained in this case are in fact far in excess of what is normally observed in practice. Therefore, if the present theory is to give reasonable results at low temperatures, it seems essential to take the scattering of phonons by lattice defects into account. It is perhaps not entirely without significance that, with what seems to be a reasonable choice for p (and the other parameters of the theory), the present theory can be brought into agreement with the measured thermoelectric force $E = \int_0^T Q dT$ of sodium at low temperatures. Curve A of Fig. 1 shows the experimental result (14), curve B the result

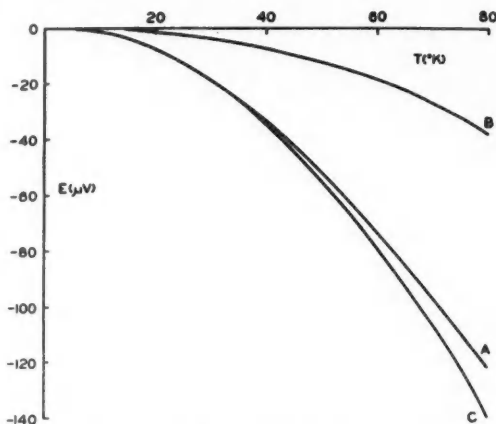


FIG. 1. The absolute thermoelectric force of sodium at low temperatures. A, experimental data; B, Q_θ ; C, $Q_e + Q_\theta$ (see text).

of the theory when Q_θ is ignored, and curve C the result of the theory when $Q = Q_e + Q_\theta$, with $p = 70$, $\Theta = 202^\circ \text{K}$., $\zeta = 3.2 \text{ eV}$., $N_a = 1$, and $\alpha_1 = \frac{2}{3}$, $\alpha_2 = \alpha_3 = \frac{1}{3}$ (the values of the α_j 's represent a rough compromise between the 'Bloch' assumption $\alpha_1 = 1$, $\alpha_2 = \alpha_3 = 0$, and the 'Makinson' (16) assumption $\alpha_1 = \alpha_2 = \alpha_3 = \frac{1}{3}$). The value of p chosen here leads to values of Q_θ

of the order of $3Q_e$, and it corresponds to a free path [14] of the same general order of magnitude as the free path which determines the thermal resistance of alkali halide crystals in the liquid hydrogen region, where scattering of phonons by lattice defects is also the predominant scattering mechanism (8).

The theory in the form given here is, of course, not sufficiently general to enable much reliance to be placed upon its quantitative predictions, and it does not explain anomalies such as the anomalous positive sign of Q observed in many metals (including monovalent ones), or the effect of small amounts of impurity in producing large increases in Q (14). A much more general theory is therefore required; in the meantime, however, it does seem worth stressing that the term Q_e which arises from the non-equilibrium of the lattice appears to play an important part in determining the thermoelectric behavior of metals, particularly at low temperatures, and that, in view of the sensitive dependence of Q_e upon the interaction mechanism whereby lattice vibrations are scattered, the theoretical predictions lead to a much greater freedom in the possible types of thermoelectric behavior than does the theory which attempts to ascribe the observed phenomena to Q_e alone.

Turning to the electrical conductivity, we find from [6] and [15] that, when phonons are supposed to be scattered by electrons only, ρ_e becomes identical with the usual expression for the ideal part ρ_i of ρ_e , so that the effective ideal resistivity $\rho_i - \rho_e$ is identically zero. This well-known result (18) arises from the fact that, in the Bloch formulation of the theory, the electron-phonon collisions leave the total wave vector of electrons and phonons invariant, so that no stationary state exists (under isothermal conditions) in the presence of an electric field if there are no other collision processes. To overcome the difficulty various collision processes not considered here have been invoked, such as the 'Umklapp processes' (19) or electron-electron collisions (20). Even without these factors, however, it turns out that quite reasonable results are obtained for the electrical resistance if the scattering of phonons by lattice defects is taken into account in the low temperature region, as in the foregoing discussion of Q (essentially the same point has been stressed by Klemens (7)). Thus, with [15] and the values of the parameters used in the evaluation of Q for sodium, the ratio ρ_e/ρ_i is found to have the values shown in Table I. It is seen that, down to about 20° K., the effect of

TABLE I
VALUES OF ρ_e/ρ_i FOR SODIUM AT LOW TEMPERATURES

T (°K.)	100	50	20	10	8	5	4
ρ_e/ρ_i	0.022	0.029	0.088	0.30	0.41	0.65	0.76

the lattice non-equilibrium is small; at lower temperatures, however, the defect scattering of phonons is no longer able to keep the lattice close to equilibrium, and ρ_e/ρ_i begins to increase rapidly with decreasing temperature. The effective ideal resistance $\rho_i - \rho_e$ therefore decreases more rapidly than

is predicted by the T^5 -law obtained when $\rho_0 = 0$, and below about 9°K . the values of $\rho_t - \rho_0$ can be fitted quite well to a T^6 -law; remarkably enough, the ideal resistance of sodium has recently been observed to vary in just this way (15, 27), though this agreement between theory and experiment may well be fortuitous (in fact the agreement is less good above 10°K ., where the observed values appear to follow the T^3 -law more closely than is predicted by the present calculations). At sufficiently low temperatures, finally, the theoretical results have to be modified to take into account the boundary scattering of lattice waves (see below).

In the case of the thermal conductivity, finally, since the expression obtained in the present theory is merely the sum of the usual electronic and lattice conductivities, the theory has nothing to add to the usual discussions (e.g. (16, 9, 6)), and no detailed discussion is necessary here. We note only that, with the parameters used above to compute Q_0 and ρ_0 for sodium, the ratio κ_0/κ_t (where κ_t is the ideal electronic thermal conductivity) is found to be 0.032 at 50°K . and 0.013 at 20°K . (decreasing to zero as T^4 for very low temperatures); these small values confirm that, in good metallic conductors, κ_0 is only a small fraction of κ_e , except possibly in highly impure specimens in which κ_e is much smaller than κ_t at the temperatures considered. Since κ_0 is negligible in pure metals, and since there are various well-known discrepancies between the observed thermal conductivity even of monovalent metals and the expression for κ_e given by the Bloch theory, it is clear that the quantitative aspects of the present theory must be treated with considerable caution; a more realistic theory would have to take into account, amongst others, refinements of the type considered by Ziman (28).

In alloys and impure metallic elements, and in poor conductors (such as bismuth) with a small free-electron density, κ_0 may form an appreciable part of the observed thermal conductivity (for recent work see (6, 22, 24, 25)). It might be worth while investigating whether any peculiarities observed in the resistive and thermoelectric behavior of substances which show an appreciable lattice thermal conductivity could be ascribed to the effect of ρ_0 and Q_0 , and, if so, to try to correlate the behavior with the observed behavior of κ_0 . It should be noted, however, (see equations [4], [6], [7], [8]) that, while κ_0 increases, ρ_0 and Q_0 in general decrease with decreasing values of N_a , so that the correlation in question may not be a particularly simple or readily observable one.

BOUNDARY SCATTERING

At sufficiently low temperatures the phonons are scattered predominantly by grain boundaries and the external boundaries of single crystal specimens. In this region, which in metals is normally reached only at temperatures of the order of a few degrees absolute or less, the free path $L(z, T)$ is a constant L_b whose value is determined by the configuration of the boundaries, and ρ_0 , κ_0 , and Q_0 are proportional to L_b . Further, $\mathcal{Q}_{j,n}$ is proportional to T in this region, so that ρ_0 varies as T^6 , κ_0 as T^3 , and Q_0 as T^4 .

Since ρ_t is proportional to T^5 , the increase in ρ_0/ρ_t (see above) cannot con-

tinue indefinitely as the temperature is lowered, and ρ_0/ρ_1 must eventually pass through a maximum and decrease towards zero (linearly for sufficiently small T). If the decrease in ρ_0/ρ_1 takes place sufficiently rapidly, from a sufficiently high maximum value, we could in principle obtain an effective ideal resistance $\rho_1 - \rho_0$ which increases with decreasing temperature (but only over a limited range of temperature). It is tempting to try to associate this possibility with the resistance minima which occur in various metals at very low temperatures (see the review by MacDonald (13)), particularly since there is some evidence (1, 17) that the observed behavior is associated with the simultaneous presence of impurities and of grain boundaries—in general qualitative agreement with what might be expected on the basis of the present theory. However, a more detailed examination of the theoretical formulae has made it appear unlikely that they can be used, at least in their present form, to reproduce anything resembling the observed behavior, so that, while the depression of the ideal electrical resistance caused by the non-equilibrium of the lattice might provide a possible mechanism of the resistance minimum, the suggestion is a highly tentative one. But in any case it is highly desirable to investigate further the influence which ρ_0 is likely to have on the electrical resistance of metals at low temperatures.

The T^3 term in the lattice thermal conductivity, which is well known, need not be discussed here, while the analogous T^3 term in the thermoelectric power is probably usually overshadowed in practice by the linear 'electronic' term. It might possibly be worth while investigating the thermoelectric behavior at very low temperatures of metals such as bismuth in which κ_0 has been observed to be size-dependent and proportional to T^3 (25), although Q_0 would be expected to play a much smaller role than κ_0 in metals in which the number of free electrons is small.

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DISCUSSION OF SONDEHEIMER'S PAPER

Mott: If your tentative explanation of the resistance minimum is correct, one would expect to find a size effect.

Klemens: According to this explanation, the minimum can only occur when the phonon mean free path due to scattering by electrons has become long enough to be comparable to the grain boundary distance, which would be well below 1° K. Dr. Sondheimer's mechanism does not therefore explain the observed minimum at helium temperature.

Gorter: Mr. A. R. de Vroomen has developed in the Kamerlingh Onnes Laboratory a very sensitive device to measure small voltages at very low temperatures, which is similar to devices developed independently by Templeton and Buck in Ottawa and M.I.T. respectively.

By periodically disturbing superconductivity in an impure tin wire, switched in series with the voltage to be measured, an a-c. current is obtained at twice the original frequency, which current is transformed and amplified in the usual ways. The accuracy is 10^{-11} volts. Thermoelectric voltages were observed in a series of tin wires using temperature differences as low as 0.1° up to about 7° K.

The results do not quite agree with those obtained by Pullan with the aid of a superconductive galvanometer in the narrow temperature range of 3.7–4.2° K.

The thermoelectric voltage per degree observed may be written as the sum of two terms, which are proportional to T and to T^3 respectively: $Q = AT + BT^3$. The first one is to be expected from the conventional quantum theory of the conduction electrons; the second one, which was not so clearly detected earlier, from the interaction between the electrons and the phonon current. Both terms vary from sample to sample, the first one being of the order of $-\frac{1}{2}T \times 10^{-8}$ volt/degree, the second one of the order of $\frac{1}{3}T^3 \times 10^{-9}$ volts/degree.

Klemens: If one may dare to give an immediate interpretation of these results presented by Professor Gorter, it appears that in the different specimens there were imperfections which scattered phonons with the same frequency dependence as the conduction electrons; that is, it seems that the phonons were scattered by dislocations. The specimens with the lowest values of B will then have had the largest number of dislocations; the fact that they are the less pure specimens seems to confirm this interpretation, for we have found in Sydney from lattice thermal conduction in alloys that impurities seem to be accompanied by dislocations even in annealed samples. It would be interesting to compare lattice thermal conductivity and thermoelectric power in the same sample.

Bhatia: Deviations from the Grüneisen-Bloch equation will also be caused by the dispersion of the lattice vibrations. I have made some calculations of this effect for sodium using rather crude approximations. Effectively the curve showing the frequency as a function of wave number was replaced by a number of straight line segments such that the corresponding frequency spectrum closely resembled the one calculated earlier for longitudinal waves (Bhatia, *Phys. Rev.* **97**, 363 1955)); in the Debye approximation of course the frequency-wave number curve is replaced by one straight line. The effect of this is to give a resistivity whose Grüneisen Θ shows a fairly sharp minimum in the neighborhood of 20° K.; thus at the minimum there is a spurious Bloch-Grüneisen region, but at temperatures below this the resistance falls much more sharply than is given by the Bloch-Grüneisen function. This minimum does not coincide with the spurious Debye region for the specific heat, since this occurs at about 7° K. Unfortunately the departure from the Bloch-Grüneisen function observed in sodium by White and Woods occurs at a considerably lower temperature than this model would suggest.

MacDonald: Following Dr. Bhatia's remarks, some people might be interested to know that a somewhat similar approach to this kind of problem has also been made by Cornish and myself (Cornish and MacDonald, *Phil. Mag.* **42**, 1406 (1951)).

THE GENERAL VARIATIONAL PRINCIPLE OF TRANSPORT THEORY¹

By J. M. ZIMAN²

1. INTRODUCTION

The solution of the Boltzmann equation is sometimes the most difficult part of the calculation of the transport properties of a physical system. In general, this is an integral equation over many variables; the solution often proceeds best by inspired guesswork rather than by well-justified analytical arguments. However, the pure mathematical theory of integral equations does provide a general theorem linking these equations with certain variational problems. Just as in the theory of partial differential equations, this theorem provides a formal method of writing down a sequence of approximate solutions converging to the correct answer. The method is of general validity, and with sufficient effort can give a practical solution to any given problem, although the labor of setting up the machinery and computing an answer is not always justified, especially when the details of the scattering processes are not known with great accuracy. The calculations of Kohler (1948, 1949a) and of Sondheimer (1950), yielding corrections to the Bloch theory of electrical conductivity of metals, are by this method, as also is the derivation by Howarth and Sondheimer (1953) of formulae for mobility in polar semiconductors.

It is usual to consider the variational method merely as a convenient mathematical device. Such an attitude robs it of most of its interest for the average physicist, who would probably prefer the whole discussion to be put in small type in an appendix. The purpose of this review is to rescue the principle from being labelled "mathematical technique", and to show that it has a considerable, easily grasped, "physical" content. Indeed, it is hoped to show that understanding of the physical interpretation of the principle can lead to more sophistication in its practical application to the solution of Boltzmann's equation in particular cases, and to some interesting generalizations which are not obvious in the purely mathematical formulation.

The key to this interpretation may be found in the paper by Kohler (1948), where it is shown that the "variational function", that is, the integral expression whose stationary property is required by the principle, is proportional to the rate of production of entropy by collision processes. But "entropy production" plays a central role in an entirely different branch of theoretical physics—the macroscopic theory of the thermodynamics of irreversible processes. The connection between the microscopic statistical theory, starting from Boltzmann's equation, and the macroscopic thermodynamic theory, where the parameters of the system are supposed known, is usually through the transport coefficients—the electrical and thermal conductivities, etc. This link is not always very firm, and may even be broken by mistake, as Sond-

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heimer (1956) has pointed out. The appearance in both theories of the same scalar quantity suggests a much more intimate relation, which should be made explicit. One recalls that it is very convenient to define the connection between *equilibrium* statistical mechanics and thermodynamics by the identification of entropy; Boltzmann's H-theorem then appears as a proof (or demonstration) of the Second Law of Thermodynamics. A variational theorem for entropy production in *non-equilibrium* statistical mechanics might thus be expected to correspond, in the same way, to a general law of steady state thermodynamics, and hence have a much greater content than as a mere mathematical theorem.

A discussion along such general lines may seem out of place in a symposium on the special topic of electron transport in solids. The excuse for opening this window on to a wider landscape is partly to look outward, to see where we are on the map, and partly to let the light inward, to show more clearly how to do the things we want to do within our own room. Arising out of detailed work in the special field of electron transport, the investigation leads us away into realms of abstract theory, but in the end we return to the particular problem with some new tools and new modes of thought.

2. THE VARIATIONAL PRINCIPLE

We shall attempt to avoid too abstract a formulation by talking in terms of a simple standard problem—the electrical conductivity of a metal containing static impurity centers. For completeness, we define a standard notation, following Wilson (1953). Boltzmann's equation is deduced from the balancing of the rates at which electrons are induced to change from one quasi-stationary state (labelled by the wave vector \mathbf{k}) to another. An electric field \mathcal{E} causes $f_{\mathbf{k}}$, the distribution function for electrons in state \mathbf{k} , to change at the rate

$$\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right]_{\text{drift}} = -\frac{e}{\hbar} \mathcal{E} \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}} \quad (1)$$

$$\approx -e \mathcal{E} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial E_{\mathbf{k}}}$$

if $f_{\mathbf{k}}$ is close to its equilibrium value $f_{\mathbf{k}}^0$. Here $\mathbf{v}_{\mathbf{k}}$ is the group velocity, and $E_{\mathbf{k}}$ the energy, in state \mathbf{k} .

On the other hand, suppose that the probability of an electron, known to be in state \mathbf{k} , being scattered into state \mathbf{k}' (known to be initially empty) lying in the volume element $d\mathbf{k}'$ in k -space, is $Q(\mathbf{k}, \mathbf{k}')d\mathbf{k}'$. Then the collision rate of change of $f_{\mathbf{k}}$ is given by

$$\left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right]_{\text{scatter}} = - \int \{ f_{\mathbf{k}}(1-f_{\mathbf{k}'})Q(\mathbf{k}, \mathbf{k}') - f_{\mathbf{k}'}(1-f_{\mathbf{k}})Q(\mathbf{k}', \mathbf{k}) \} d\mathbf{k}'.$$

We take account here of the exclusion principle.

In (2) we have distinguished explicitly between $Q(\mathbf{k}, \mathbf{k}')$ and $Q(\mathbf{k}', \mathbf{k})$ which is the measure of the inverse scattering process, from \mathbf{k}' to \mathbf{k} . According to the principle of microscopic reversibility, these two functions are equal, i.e.

$$Q(\mathbf{k}, \mathbf{k}') = Q(\mathbf{k}', \mathbf{k}). \quad (3)$$

This symmetry is an essential point in what follows.

It is convenient to define a new function, $\Phi_{\mathbf{k}}$, which is a measure of the deviation of $f_{\mathbf{k}}$ from equilibrium. We write

$$\begin{aligned} f_{\mathbf{k}} &= f_{\mathbf{k}}^0 - \Phi_{\mathbf{k}} \partial f_{\mathbf{k}}^0 / \partial E_{\mathbf{k}} \\ (4) \qquad &= f_{\mathbf{k}}^0 + \Phi_{\mathbf{k}} f_{\mathbf{k}}^0 (1 - f_{\mathbf{k}}^0) / kT \end{aligned}$$

by direct differentiation of $f_{\mathbf{k}}^0$ which is a Fermi function depending only on $E_{\mathbf{k}}$.

Adding (1) and (2) to get the total rate of change of $f_{\mathbf{k}}$, which must be zero in the steady state, and using (3) and (4), we obtain the Boltzmann equation in the following form:

$$(5) \qquad -e \mathcal{E} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial E_{\mathbf{k}}} = \frac{1}{kT} \int (\Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'}) P(\mathbf{k}, \mathbf{k}') d\mathbf{k}'.$$

In this formulation we must define a new probability function,

$$(6) \qquad P(\mathbf{k}, \mathbf{k}') = f_{\mathbf{k}}^0 (1 - f_{\mathbf{k}'}^0) Q(\mathbf{k}, \mathbf{k}'),$$

which gives the scattering rate, in the equilibrium state, between \mathbf{k} and \mathbf{k}' , that is, subject to the probability, $f_{\mathbf{k}}^0$, of \mathbf{k} being actually occupied and, $(1 - f_{\mathbf{k}'}^0)$, of \mathbf{k}' being unoccupied, at any given moment. This function is also symmetric, i.e.

$$(7) \qquad P(\mathbf{k}, \mathbf{k}') = P(\mathbf{k}', \mathbf{k}).$$

This follows directly from (3), remembering that energy is conserved in the process so that $f_{\mathbf{k}}^0 = f_{\mathbf{k}'}^0$. Alternatively, (7) is merely a special case of the principle of detailed balance.

Some care has been taken here to establish a notation which will be suitable for later discussion of more complex cases, although it is perhaps a little more formal than is necessary for the present simple problem.

In principle, we know the left-hand side of (5) and the kernel $P(\mathbf{k}, \mathbf{k}')$; the Boltzmann equation is thus an inhomogeneous integral equation for the unknown distribution function $\Phi_{\mathbf{k}}$. It belongs to a class of equations which may be represented in the simplest form by

$$\begin{aligned} X(k) &= \int \{ \Phi(k) - \Phi(k') \} P(k, k') dk' \\ (8) \qquad &= L\Phi \end{aligned}$$

where $X(k)$ is a known function and $P(k, k')$ is a known symmetric kernel. To apply the variational principle, one other fact is needed; $P(k, k')$ must always be of the same sign. This is a natural property of (6) since $P(\mathbf{k}, \mathbf{k}')$ is a probability, and hence always positive. We suppose, therefore, that $P(k, k')$ is positive definite in (8).

For compactness of notation we have introduced the symbol L for the integral operator in (8), acting on Φ . We also introduce the convention

$$(9) \qquad \langle \Phi, \Psi \rangle \equiv \int \Phi(k) \cdot \Psi(k) dk$$

which is equivalent to defining an "inner product" of the functions.

The variational principle may now be stated. There are a number of different forms, of which the following is typical (e.g. Wilson 1953):

1. Let Φ be the solution of the integral equation (8) and Ψ any function for which

$$(10) \quad \langle \Psi, L\Psi \rangle = \langle \Psi, X \rangle.$$

Then, of all functions Ψ satisfying this relation, Φ is the one which makes $\langle \Psi, L\Psi \rangle$ a maximum.

The proof is quite simple. In its barest terms, we have

$$\begin{aligned} \langle \Psi, L\Phi \rangle &= \iint \Psi(k) P(k, k') \{ \Phi(k) - \Phi(k') \} dk dk' \\ (11) \quad &= \iint \Psi(k') P(k, k') \{ \Phi(k') - \Phi(k) \} dk dk' \end{aligned}$$

from the symmetry of $P(k, k')$. Adding gives

$$\begin{aligned} \langle \Psi, L\Phi \rangle &= \frac{1}{2} \iint \{ \Psi(k) - \Psi(k') \} P(k, k') \{ \Phi(k) - \Phi(k') \} dk dk' \\ (12) \quad &= \langle \Phi, L\Psi \rangle \end{aligned}$$

from the symmetry of the integral as between Φ and Ψ .

Moreover, putting $\Phi = \Psi$, we obtain an integral with a square and a positive definite function in the integrand, i.e., for any Ψ

$$(13) \quad \langle \Psi, L\Psi \rangle \geq 0.$$

Condition (10) and the fact that Φ satisfies the integral equation (8) give

$$(14) \quad \langle \Psi, L\Phi \rangle = \langle \Psi, X \rangle = \langle \Psi, L\Psi \rangle.$$

From (13) we have

$$\begin{aligned} 0 &\leq \langle (\Phi - \Psi), L(\Phi - \Psi) \rangle \\ &= \langle \Phi, L\Phi \rangle + \langle \Psi, L\Psi \rangle - \langle \Phi, L\Psi \rangle - \langle \Psi, L\Phi \rangle \\ &= \langle \Phi, L\Phi \rangle + \langle \Psi, L\Psi \rangle - 2\langle \Psi, L\Phi \rangle, \text{ from (12),} \\ &= \langle \Phi, L\Phi \rangle - \langle \Psi, L\Psi \rangle, \text{ from (14),} \end{aligned}$$

i.e.

$$(15) \quad \langle \Phi, L\Phi \rangle \geq \langle \Psi, L\Psi \rangle,$$

which we are required to prove.

The theorem is used as follows. We suppose that Φ may be expanded in a series of the form

$$(16) \quad \Phi(k) = \sum_n a_n \phi_n(k)$$

where $\phi_n(k)$ are known functions of k , making up, perhaps, a complete sequence, whilst the variables a_n are supposed to be chosen later to make Φ the solution of the integral equation. But substituting into the integral expressions $\langle \Phi, L\Phi \rangle$ and $\langle \Phi, X \rangle$ yields formulae containing integrals of the form $\langle \phi_n, L\phi_m \rangle$ and $\langle \phi_n, X \rangle$ which are coefficients of quadratic and linear forms in a_n . The principle is then applied to give the best choice of a_n , by differentiation with respect to these variables, making the variational function a maximum subject to the subsidiary condition (10). This yields a set of linear equations, which can be solved by simple algebra. Of course, we

need an infinite sequence to obtain an exact solution of the integral equation, but by careful choice of the functions $\phi_n(k)$ we may usually get a good approximation to the answer with only a few terms. Crudely speaking, the art of guessing the functional form of the solution of the equation is refined and extended, at the cost of a certain amount of algebra and arithmetic, in a systematic way. From the solution thus obtained, the transport coefficients may be calculated in the usual manner.

3. ENTROPY PRODUCTION

Having stated the principle in its simplest form, as a mathematical theorem, we now consider the physical approach. If we look back from (8) to (5), that is, from the basic simplified integral equation to the Boltzmann equation of which it is a model, we see that the analogue of the variational function (i.e., in the condensed notation, $\langle \Phi, L\Phi \rangle$) must be the expression obtained by multiplying the right-hand side of (5) by $\Phi_{\mathbf{k}}$ and integrating with respect to \mathbf{k} . In other words, the variation process is to be applied to

$$(17) \quad \frac{1}{kT} \int \Phi_{\mathbf{k}} \int (\Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'}') P(\mathbf{k}, \mathbf{k}') d\mathbf{k} d\mathbf{k}' = - \int \Phi_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial t} \Big|_{\text{scatter}} d\mathbf{k}.$$

But let us consider the statistical definition of entropy (e.g. ter Haar, 1954) in a Fermi-Dirac assembly, assuming without proof that this is valid in non-equilibrium states:

$$(18) \quad S = -k \int \{f_{\mathbf{k}} \ln f_{\mathbf{k}} + (1-f_{\mathbf{k}}) \ln(1-f_{\mathbf{k}})\} d\mathbf{k}.$$

Let this equation be differentiated with respect to time, and let us assume that we are near equilibrium, so that $f_{\mathbf{k}}$ is close to $f_{\mathbf{k}}^0$ and the formula need be expanded only to the lowest power of $\Phi_{\mathbf{k}}$. A little manipulation yields the following:

$$(19) \quad \frac{\partial S}{\partial t} = -\frac{1}{T} \int \Phi_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial t} d\mathbf{k} + \frac{1}{kT^2} \int E_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial t} d\mathbf{k}.$$

The second term may be dropped, since it is proportional to the rate of change of the total energy of the system, and this is zero for the type of collisions we are considering. In the steady state, of course, the over-all rate of change of $f_{\mathbf{k}}$ is also zero, so that the distribution is stationary and has constant entropy. But if we consider separately the two equal and opposite contributions to this rate of change, from drift and collisions respectively, we may infer two corresponding contributions to the production of entropy, i.e. for the scattering terms,

$$(20) \quad \frac{\partial S}{\partial t} \Big|_{\text{scatter}} = -\frac{1}{T} \int \Phi_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial t} \Big|_{\text{scatter}} d\mathbf{k}.$$

Reference back to (17) shows that, apart from a constant factor $1/T$, this is just the variational function that we proposed for the Boltzmann equation. By the basic symmetry of $P(\mathbf{k}, \mathbf{k}')$, and with the same argument as for (12), we may write this expression in the particularly elegant form

$$(21) \quad \left. \frac{\partial S}{\partial t} \right]_{\text{scatter}} = \frac{1}{2kT^2} \iint (\Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'})^2 P(\mathbf{k}, \mathbf{k}') \, d\mathbf{k} \, d\mathbf{k}'.$$

This is the result proved by Kohler. From it we see that the effect of collisions is always to increase the entropy, in agreement with the Second Law of Thermodynamics.

In addition to the integral $\langle \Psi, L\Psi \rangle$ in (10), there also occurs the expression $\langle \Psi, X \rangle$. It will be remembered that $X(\mathbf{k})$ is the known function on the left of the integral equation; from the way we derived the Boltzmann equation, we see that the analogue of $\langle \Phi, X \rangle$ is just

$$(22) \quad \begin{aligned} -\frac{1}{T} \int \Phi_{\mathbf{k}} e\mathcal{E} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial E_{\mathbf{k}}} \, d\mathbf{k} &= \frac{1}{T} \int \Phi_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial t} \Big|_{\text{drift}} \, d\mathbf{k} \\ &= -\left. \frac{\partial S}{\partial t} \right]_{\text{drift}}, \end{aligned}$$

that is, minus the rate at which entropy changes as a result of drift. In fact, since (22) must equal (21), the effect of the electric field is to reduce the entropy in the material, tending always to produce more order in the electron distribution.

It is interesting to verify that (22) actually does represent entropy production in macroscopic terms. From (22) and (4) we have

$$(23) \quad \begin{aligned} -\left. \frac{\partial S}{\partial t} \right]_{\text{drift}} &= \frac{1}{T} \mathcal{E} \cdot \int e\mathbf{v}_{\mathbf{k}} (f_{\mathbf{k}} - f_{\mathbf{k}}^0) \, d\mathbf{k} \\ &= \frac{1}{T} \mathcal{E} \cdot \mathcal{J}, \end{aligned}$$

where \mathcal{J} is the electric current* in the steady state. This is exactly what we should write for the production of entropy in the form of Joule heat, for the current \mathcal{J} flowing down the electric field \mathcal{E} at temperature T . We may look upon the whole irreversible transport process as the production of entropy, at rate (21), by scattering inside the material, and the subsequent removal of the same amount of entropy (leaving the material in the steady state of constant entropy) by the electric field, sweeping it into the reservoirs which maintain isothermal conditions, where it appears in precisely the amount we should calculate from macroscopic thermodynamics.

4. THERMODYNAMIC FORMULATION

In the theory of the thermodynamics of irreversible processes, entropy production also enters, according to the following formula (e.g. de Groot 1951):

$$(24) \quad \frac{\partial S}{\partial t} = \sum_k X_k J_k \quad (k = 1, 2, \dots, n, \text{ say})$$

which defines the generalized thermodynamics "forces", X_k , conjugate to a given set of generalized "currents", J_k . In order to interpret the variational

*Strictly speaking, it is the current *density* multiplied by the volume, but we shall assume throughout that we are dealing with a unit cube, in which there is no difference between current and current density, entropy and entropy density, etc.

principle in this language, we must find entities to which we may give these names. It is clear that the distribution function, $\Phi_{\mathbf{k}}$, is the analogue of a current, for by summation with suitable scale factors, as in (23), over all the states \mathbf{k} , it yields the actual macroscopic current. We may think of $\Phi_{\mathbf{k}}$ as measuring the actual, net, out-of-balance flux of electrons in the \mathbf{k} th state, just as if it were the current, J_k , in the k th branch of an electrical circuit. Correspondingly, from (22) and (24), the generalized force conjugate to $\Phi_{\mathbf{k}}$ must be

$$(25) \quad X_{\mathbf{k}} = -\frac{1}{T} e \mathcal{E} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial E_{\mathbf{k}}}.$$

It is only necessary to think of the integral over \mathbf{k} as a sum, which it strictly is in a finite specimen, to make the correspondence complete.

Let us first translate the Boltzmann equation, (5), into this language. We may write it, for the present purpose, in the form

$$(26) \quad X_{\mathbf{k}} = \int L(\mathbf{k}, \mathbf{k}') \Phi_{\mathbf{k}'} d\mathbf{k}'$$

where the kernel $L(\mathbf{k}, \mathbf{k}')$ is compounded in an obvious way out of $P(\mathbf{k}, \mathbf{k}')$, etc., and has the same symmetry and sign properties. This is equivalent to writing

$$(27) \quad X_k = \sum_{k'} L_{kk'} J_{k'},$$

i.e., the relationship between the forces and currents is linear, with the coefficients $L_{kk'}$. Moreover, from the properties of $L(\mathbf{k}, \mathbf{k}')$ we may infer that the coefficients $L_{kk'}$ form a positive definite symmetric matrix. These statements are none other than the principles proposed by Onsager, as the foundation of the standard thermodynamic theory. The symmetry relations

$$(28) \quad L_{kk'} = L_{k'k}$$

are the famous Onsager relations. It is clear that our interpretation of the steady state is consistent with this essential principle.

Now to the main business, which is to find a rule for deducing these relations. Look again at (21), which defines the entropy production due to collisions. This is a quadratic function of $\Phi_{\mathbf{k}}$. A given set of currents forced through an array of scattering centers or other dissipative devices gives rise to a definite amount of entropy, independently of how those currents are created. We write

$$(29) \quad \left. \frac{\partial S}{\partial t} \right]_{\text{scatter}} = \sum_{kk'} L_{kk'} J_k J_{k'} = \left. \frac{\partial S}{\partial t} \right]_{\text{in}}$$

to show the quadratic dependence, using (26) and (27). We call this the *intrinsic*, or *internal* entropy production, because it depends only on the local properties, local currents, etc.

On the other hand, we already have formula (24), which corresponds to (22) and (23). We call this the *extrinsic* entropy production

$$(30) \quad -\left. \frac{\partial S}{\partial t} \right]_{\text{drift}} = \sum_k X_k J_k = \left. \frac{\partial S}{\partial t} \right]_{\text{ex}}$$

since it can be calculated from measurements made outside the system, determining the forces and currents, and does not depend on the local behavior of the electrons nor on the way in which they are scattered.

But we have seen that (29) and (30) correspond to the functions introduced in the statement and proof of the variational principle I, that is, to $\langle \Phi, L\Phi \rangle$ and $\langle \Phi, X \rangle$ in (10). Gathering together the various threads, we construct the following statement of the principle:

II. Consider all distributions of currents such that the intrinsic entropy production equals the extrinsic entropy production for the given set of forces. Then, of all current distributions satisfying this condition, the steady state distribution makes the intrinsic entropy production a maximum.

The proof for the Boltzmann equation goes without further logic than the interpretation of the language into the formalism of principle I. The same proof implies that (27) may be derived from the same principle, and from the definitions (29) and (30). The symmetry relation (28) is an obvious consequence of the fact that the intrinsic entropy production (29) is *defined* as a quadratic form in the current variables, and therefore automatically has symmetric coefficients.

It will be seen, however, that we have now what appears to be a general principle of the thermodynamics of irreversible processes. Put briefly, we say that, in a system subject to fixed forces, the currents will distribute themselves so as to make the entropy production by internal dissipative processes a maximum, subject only to the condition that this must equal the production of entropy estimated from external measurements of these currents and forces. The actual result we have deduced from a special case, but the statement II is in general terms. The fact is that this is a known general principle (although for some reason it is not given in any of the books on the subject). It was deduced by Onsager (1931) from general statistical arguments, and was precisely the basis of his derivation of the Onsager relations (28).

In a restricted form, the principle is much older. For example, it is closely related to Rayleigh's theorem involving the dissipation function (Rayleigh 1896). Perhaps the most familiar case is the theorem concerning the distribution of currents, J_k , in a network of resistances $L_{kk'}$ with given applied electromotive forces, X_k . This requires that the currents be such that

$$(31) \quad \sum_{kk'} L_{kk'} J_k J_{k'} - 2 \sum_k J_k X_k$$

is a minimum (Jeans 1920). The principle, II, as we have written it, is not quite the same as this, although it is mathematically equivalent. For example, in (31) there is a function to be *minimized*, whereas II refers to the *maximum* of the entropy production. If we look at (31), we see that it corresponds to

$$(32) \quad \left[\frac{dS}{dt} \right]_{\text{in}} - 2 \left[\frac{dS}{dt} \right]_{\text{ex}},$$

which is, in the steady state, just the *negative* of the actual production of entropy in the dissipation process. This is also the form of the theorem stated by Onsager.

An alternative statement, also easily proved (e.g. Wilson 1953), is that we must minimize

$$(33) \quad \sum_{kk'} L_{kk'} J_k J_{k'} / \left(\sum_k J_k X_k \right)^2 = \frac{dS}{dt} \Big|_{\text{in}} / \left\{ \frac{dS}{dt} \Big|_{\text{ex}} \right\}^2$$

with respect to the currents. This expression reduces to the *inverse* of the actual entropy production in the steady state, so that a minimum might be expected. The form of the principle given in I and II seems the most natural from a physical point of view, though not necessarily the most concise mathematical formulation.

The various formulations have been noted explicitly, because there is danger of confusion with another theorem where entropy production is extremal. This is Prigogine's theorem, which states, crudely speaking, that if not all the forces acting on a system are fixed the free forces will take such values as to make the entropy production a minimum. Taking for granted the linear relations (22) between forces and currents, it tells us what to expect when we let go of some of the leads, and allow the potentials to seek their own levels. The two theorems seem to be entirely independent of one another.

5. PRACTICAL ADVANTAGES OF THE GENERAL PRINCIPLE

Although there is some amusement in unmasking the mathematical theorem, and denouncing it as a mere "physical principle", our real business is to show that this approach to the problem has practical advantages in the actual calculation.

In the first place, entropy and entropy production are good physical quantities, more or less easily defined for any given system. It is thus an easy matter to find the special variational principles in detailed mathematical terms, for Boltzmann equations of any degree of complexity. For example, consider the case of phonon-electron scattering, as in the Bloch model, but allowing for some deviation from equilibrium in the phonon distribution. If there is also a thermal gradient ∇T , we must solve the following equations:

$$(34) \quad \left\{ \begin{aligned} -e\mathcal{E} \cdot \mathbf{v}_k \frac{\partial f_k^0}{\partial E_k} - \mathbf{v}_k \cdot \nabla T \frac{\partial f_k^0}{\partial T} &= \frac{1}{kT} \iint (\Phi_k + \Phi_p - \Phi_{k'}) P_{k\mathbf{p}}^{\mathbf{k}'} d\mathbf{k}' d\mathbf{p} \\ &+ \frac{1}{kT} \iint (\Phi_k - \Phi_p - \Phi_{k'}) P_{k\mathbf{p}}^{\mathbf{p}\mathbf{k}'} d\mathbf{k}' d\mathbf{p}; \\ -\mathbf{v}_p \cdot \nabla T \frac{\partial N_p^0}{\partial T} &= \frac{1}{kT} \iint (\Phi_k + \Phi_p - \Phi_{k'}) P_{k\mathbf{p}}^{\mathbf{k}'} d\mathbf{k}' d\mathbf{k}. \end{aligned} \right.$$

Here N_p^0 is the equilibrium distribution function (Bose-Einstein) for phonons of wave vector \mathbf{p} . Φ_p has much the same significance as Φ_k , except that the Bose-Einstein statistics give, instead of (4),

$$(35) \quad N_p = N_p^0 + \Phi_p N_p^0 (1 + N_p^0) / kT$$

for the out-of-balance distribution.

The probability function $P_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'}$ for the process by which electron \mathbf{k} absorbs phonon \mathbf{p} and goes into state \mathbf{k}' is defined by

$$(36) \quad P_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'} = Q_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'} f_{\mathbf{k}}^0 N_{\mathbf{p}}^0 (1 - f_{\mathbf{k}'}^0) = P_{\mathbf{k}'}^{\mathbf{k}\mathbf{p}}$$

where $Q_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'}$ is the corresponding scattering probability when the initial states are known to be singly occupied and the final state is initially empty. The essential symmetry of $P_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'}$ for the forward and reverse processes may be proved in detail from the form of the distribution functions, from conservation of energy, and from microscopic reversibility (which imposes the same symmetry on $Q_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'}$). Here also, the principle of detailed balance gives an equivalent proof.

In calculating the entropy production, it is necessary to include the contribution of the phonons, which comes out, just as in (20), to

$$(37) \quad -\frac{1}{T} \int \Phi_{\mathbf{p}} \frac{\partial N_{\mathbf{p}}}{\partial t} d\mathbf{p}.$$

Using the symmetry properties of $P_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'}$ we find, altogether,

$$(38) \quad \left[\frac{\partial S}{\partial t} \right]_{\text{in}} = \frac{1}{kT^2} \iiint (\Phi_{\mathbf{k}} + \Phi_{\mathbf{p}} - \Phi_{\mathbf{k}'})^2 P_{\mathbf{k}\mathbf{p}}^{\mathbf{k}'} d\mathbf{k} d\mathbf{p} d\mathbf{k}',$$

which must be the variational function of our problem. No doubt this formula might have been guessed, but it is not immediately obvious by inspection of (34). It is easy to suggest any further generalizations, for scattering processes involving more and more particles.

Equation (38) provides a convenient starting point for the calculation of the effect of the phonon unbalance, which is discussed by Sondheimer in another paper in this series. It also represents, as it happens, the simplest approach to the original Bloch calculation, where $\Phi_{\mathbf{p}}$ is taken to be zero. The standard approach to this (e.g. Wilson 1953) is through the Bloch integral equation, derived from (34) by the assumption that

$$(39) \quad \Phi_{\mathbf{k}} = c(E_{\mathbf{k}}) k_z$$

where k_z is the component of \mathbf{k} in the field direction and $c(E_{\mathbf{k}})$ is a function to be determined later by the solution of the integral equation.

The Bloch equation, as all will know who have attempted to use it, is extremely complicated, running to several lines of type in its simplest formulation. In the end, it is necessary to use the variational method to obtain an exact solution (Sondheimer 1950), introducing as a set of trial functions for $c(E)$ the various powers of E . We might just as well have used the corresponding set of trial functions for $\Phi_{\mathbf{k}}$ in the Boltzmann equation itself, with the variational function (38). It turns out that the integrals are much easier to evaluate, and the same solutions may be found with considerably less work. One can see, for example, that it is not necessary to count separately the processes in which a phonon is emitted and those in which it is absorbed; these have the same elementary probability, and correspond merely to forward and reverse directions of the process $\mathbf{k} + \mathbf{p} \rightleftharpoons \mathbf{k}'$. Again, because \mathbf{k} , \mathbf{k}' , and \mathbf{p} all

appear on the same footing in the integrals, one may carry out the integration in whatever order is most convenient. The easiest way is to remove the integral over \mathbf{p} by conservation of momentum, then to integrate over the energy of \mathbf{k} using energy conservation, next to integrate over $E_{\mathbf{k}}$ using the properties of the Fermi functions, and finally to consider the various orientations of the wave vectors \mathbf{k} and \mathbf{k}' on the Fermi surface. This order of integration is impossible in the Bloch integral equation, all of whose complexity arises from treating the angular variation of \mathbf{k} much too early.

It would take us too far afield to demonstrate these results in detail. It is sufficient to say that the method has been used to derive the standard formulae for a wide range of problems in the theory of metals and semiconductors, and in every case the algebraic work is much shorter than in the conventional derivations. These include the corrections to the Bloch formulae (Sondheimer 1950), the extension to include Umklapp processes (Ziman 1954), inelastic electron scattering in rare earth metals (Elliott 1954) and its contribution to thermal resistance and thermoelectric properties, scattering of carriers by optic modes in polar semiconductors (Howarth and Sondheimer 1953), and the contribution of scattering by dislocations to the electrical resistance of a metal (Mackenzie and Sondheimer 1950; Hunter and Nabarro 1953).

The moral is that entropy is a scalar physical quantity, which may be defined in a very general way irrespective of the choice of representation. Entropy production, also, cannot depend on any special way of counting collision processes, nor on the choice of lattice directions for axes, and so on. That is, it has the properties of a mathematical invariant of the problem; it is the fixed center about which various coordinate systems and representations pivot. By using these properties explicitly, we have the opportunity, at the last possible moment, of choosing any special frame of reference which will make the final stages of the calculation as simple as possible.

6. EXPLOITING THE LINK WITH THERMODYNAMICS

Another practical advantage of the general method is that we may avoid a number of routine steps in obtaining the transport coefficients from the solution of the Boltzmann equation, and write down directly some general formulae without special models. This method is used on several occasions by Kohler and his co-workers. To illustrate the technique, we shall consider the problem of the conduction of heat by phonons in an insulating solid.

In general we must take account of two types of scattering process—direct scattering by impurities, imperfections, etc., and phonon-phonon interactions (Peierls 1955) in which $\mathbf{p} + \mathbf{p}' \rightleftharpoons \mathbf{p}''$. The former we may suppose to go with probability $P(\mathbf{p}, \mathbf{p}')$ and the latter with probability $P_{\mathbf{p}\mathbf{p}'}^{\mathbf{p}''}$, these quantities being defined just as in the previous cases. It is obvious that the entropy production corresponding to the distribution $\Phi_{\mathbf{p}}$ is given by

$$(40) \quad \left. \frac{dS}{dt} \right|_{\text{in}} = \frac{1}{2kT^2} \iint (\Phi_{\mathbf{p}} - \Phi_{\mathbf{p}'})^2 P(\mathbf{p}, \mathbf{p}') d\mathbf{p} d\mathbf{p}' \\ + \frac{1}{kT^2} \iiint (\Phi_{\mathbf{p}} + \Phi_{\mathbf{p}'} - \Phi_{\mathbf{p}''})^2 P_{\mathbf{p}\mathbf{p}'}^{\mathbf{p}''} d\mathbf{p} d\mathbf{p}' d\mathbf{p}''.$$

(We should be careful to allow for the various polarizations, but this is trivial.)

Now, Φ_p corresponds to a distribution in which there will be a thermal current flowing, of amount

$$(41) \quad U = - \int E_p v_p \Phi_p \frac{\partial f_p^0}{\partial E_p} dp.$$

This current flowing down the temperature gradient ∇T represents a dissipative process in which entropy is produced at the rate

$$(42) \quad \left. \frac{dS}{dt} \right]_{ex} = - \nabla T \cdot U / T^2 \\ = U^2 / \kappa T^2$$

where κ is the thermal conductivity of the medium (assumed isotropic). In the steady state, the entropy production by collisions equals the extrinsic macroscopic production, so that (40) and (42) are equal. We have at once from (41)

$$(43) \quad \frac{1}{\kappa} =$$

$$\frac{\frac{1}{2kT^2} \iint (\Phi_p - \Phi_{p'})^2 P(p, p') dp dp' + \frac{1}{kT^2} \iiint (\Phi_p + \Phi_{p'} - \Phi_{p''})^2 P_{pp''} dp dp' dp''}{\left\{ -\frac{1}{T} \int E_p v_p \Phi_p \frac{\partial f_p^0}{\partial E_p} dp \right\}^2}$$

for the value of the thermal resistivity.

Of course, this formula is meaningless unless Φ_p represents a true stationary state, and is a solution of the Boltzmann equation; we cannot avoid that part of the calculation. However, the variational principle may be used here to very practical advantage. The denominator of (43) is $(U/T)^2$. But, from (41), we may write

$$(44) \quad U/T^2 = \left. \frac{dS_1}{dt} \right]_{ex}$$

where the right-hand side means "the entropy production when the current U flows down the thermal gradient $\nabla T = 1$ ". Thus (43) is a ratio of the form

$$(45) \quad \frac{1}{\kappa} = \frac{1}{T^2} \left. \frac{dS}{dt} \right]_{in} / \left\{ \left. \frac{dS_1}{dt} \right]_{ex} \right\}^2$$

which is nearly the same as occurs in (33), except that we choose the particular value unity for the thermal gradient and are thus interested in definite values for the thermodynamic forces.

It was remarked that the variational principle asserts that in the steady state the ratio (33) takes its minimum value. Thus, (43) is not merely an expression for $1/\kappa$ to be used when we have found Φ_p by other means; it is a quantity which is always greater than or equal to the true thermal resistivity, the closeness of $1/\kappa$ depending on the closeness of Φ_p to the true distribution. If we use the "inner product" notation, and consider the ratio in the form

$$(46) \quad \langle \Phi, L\Phi \rangle / \{ \langle \Phi, X \rangle \}^2, \text{ with } X = 1,$$

we are reminded of the variational principle in quantum mechanics, in the form that the expectation value of the energy in any state ϕ , i.e.

$$(47) \quad \int \phi^* \mathfrak{H} \phi d\tau / \int \phi^* \phi d\tau,$$

is always greater than or equal to the energy of the ground state of the system, the difference depending on the degree to which ϕ approximates to the ground-state wave function. We may think of the resistivity as the "expectation value" of the scattering operator L in the non-equilibrium state Φ , suitably normalized. The rule that the value of the energy estimated from (47) is always better than the approximation in the choice of ϕ will also hold in the present argument.

This formulation is particularly useful because in many cases we use just a single trial function to establish an approximate result, without bothering to compute a complete solution. In that case we shall know at once the sign of the error, and (43) contains the absolute minimum number of integrals that need to be evaluated, with no further algebraic steps to write down the transport coefficients. More complicated cases (for example, thermoelectric power in metals) can be represented similarly, and explicit formulae for the exact values of the transport coefficients (that is, using a complete sequence of trial functions, as in (16)) can be written down in terms of matrices with elements of the form $\langle \phi_n, L\phi_m \rangle$, etc. The employment of such general formulae for the transport coefficients avoids the danger, pointed out by Sondheimer (1956), of making inconsistent approximations in the calculation of the separate coefficients. For example, the Onsager relations are automatically satisfied.

7. A FORMULA IN THE THEORY OF LATTICE CONDUCTION

We have considered the case of phonon-phonon interaction because one can derive a formula of considerable interest and utility whose proof seems very difficult except by the present argument. We therefore digress for a moment from the general discussion, to give this derivation.

It is well known (Peierls 1955) that a system in which there are only phonon-phonon processes in which momentum is conserved (N-processes) would have infinite thermal conductivity. This follows at once from (43), by writing

$$(48) \quad \Phi_{\mathbf{p}} = \mathbf{p} \cdot \mathbf{u}$$

where \mathbf{u} is some arbitrary vector. Suppressing $P(\mathbf{p}, \mathbf{p}')$ for the moment, we obtain in the denominator only

$$(49) \quad \frac{1}{kT^2} \iiint \{ (\mathbf{p} + \mathbf{p}' - \mathbf{p}'') \cdot \mathbf{u} \}^2 P_{\mathbf{p}\mathbf{p}'} \mathbf{p}'' d\mathbf{p} d\mathbf{p}' d\mathbf{p}''$$

which vanishes if $\mathbf{p} + \mathbf{p}' = \mathbf{p}''$. Hence, (48) must be the solution of the Boltzmann equation, since it makes the ratio for $1/\kappa$ take its lowest possible value, that is, zero.

But now suppose that there are other scattering processes, as assumed in (43). If these are not very effective compared with the N-processes, it is reasonable to choose, as a first approximation trial function, just the same expression (48). The contribution of N-processes still vanishes, but there will be a contribution by impurities, etc., proportional to

$$(50) \quad \frac{1}{2kT^2} \iint \{ (\mathbf{p} - \mathbf{p}') \cdot \mathbf{u} \}^2 P(\mathbf{p}, \mathbf{p}') d\mathbf{p} d\mathbf{p}'.$$

A Debye model for the phonon modes, and the assumption that $P(\mathbf{p}, \mathbf{p}')$ does

not depend on the absolute orientation of the vectors \mathbf{p} and \mathbf{p}' , yields the following formula for the thermal resistivity:

$$(51) \quad W_i = \frac{3}{c^2} \int \frac{c_p}{v_p l_p} dp$$

where c_p is the contribution to the total specific heat, c , of the modes of wave vector p (i.e. $c = \int c_p dp$); l_p is the mean free path of these same phonons for this type of scattering, i.e.

$$(52) \quad \frac{1}{l_p} = \frac{1}{v_p} \int (1 - \cos \theta) Q_p(\theta) d\Omega$$

where $Q_p(\theta)d\Omega$ is the probability that a phonon of wave vector p is scattered through the angle θ into the solid angle $d\Omega$.

In the approximation we are using, W_i is additive for various types of scattering, so that Matthiessen's rule is assumed. The formula is extremely useful, because it is easy to calculate and offers no convergence difficulties. It has been used for various calculations, for example the scattering of phonons by electrons in semiconductors (Ziman 1956) and by isotopic mixtures (Berman, Foster, and Ziman, to be published). It is not, of course, exact, and gets worse as the scattering effect gets larger and N-processes no longer dominate the distribution function. In that case we may take it only as an upper bound to the true resistivity, and must calculate more deeply.

Finally, the effect of Umklapp processes (U-processes) can also be estimated. For these, (49) does not vanish, but contains just the square of $\mathbf{K} \cdot \mathbf{u}$ where \mathbf{K} is a reciprocal lattice vector. This is exactly the method used by Leibfried and Schlömann (1954) to calculate W_U , the contribution of the U-processes to the thermal resistivity of a dielectric solid.

8. PHENOMENA IN A MAGNETIC FIELD

The discussion so far has been mainly a review of the ideas implicit in Kohler's original paper, and mention of the various applications of the method that have actually been made. We now introduce an entirely new and in some respects puzzling problem, which is at present being studied by Mr. F. Garcia-Moliner and the author.

Suppose that to our original model of electrons scattered by static obstacles we add a magnetic field \mathbf{H} . If the field is not too large to upset our original quantization scheme, the Boltzmann equation (5) acquires an extra term on the left, i.e.

$$(53) \quad \left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right]_{\text{mag}} = -\frac{e}{\hbar} (\mathbf{v}_{\mathbf{k}} \wedge \mathbf{H}) \cdot \nabla_{\mathbf{k}} f_{\mathbf{k}}.$$

The substitution (4) for $f_{\mathbf{k}}$ gives no term from $f_{\mathbf{k}}^0$, so that we must use the full expression. Eliminating unnecessary complexity by the symbolism of (26), we may write the Boltzmann equation schematically in the form

$$(54) \quad X_{\mathbf{k}} = \int L(\mathbf{k}, \mathbf{k}') \Phi_{\mathbf{k}'} d\mathbf{k}' + M(\mathbf{H}) \Phi_{\mathbf{k}}$$

where the "magnetic scattering operator" is defined by

$$(55) \quad M(\mathbf{H}) = \frac{e}{\hbar T} \frac{\partial f_{\mathbf{k}}^0}{\partial E_{\mathbf{k}}} (\mathbf{v}_{\mathbf{k}} \wedge \mathbf{H}) \cdot \mathbf{v}_{\mathbf{k}}.$$

The general effect of the magnetic field thus appears similar to that of the scattering obstacles. The electrons are deflected as they come into contact with the magnetic lines of force. There is an important difference; in magnetic deflection all the electrons are bent round together, and the ordering of the distribution is not changed directly. This is made clear if we calculate the entropy produced by the magnetic field, using (20) and (53). We write

$$(56) \quad \left. \frac{dS}{dt} \right]_{\text{mag}} = \int \Phi_{\mathbf{k}} M(\mathbf{H}) \Phi_{\mathbf{k}} d\mathbf{k} \\ = \frac{e}{\hbar T} \int \Phi_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial E_{\mathbf{k}}} (\mathbf{v}_{\mathbf{k}} \wedge \mathbf{H}) \cdot \mathbf{v}_{\mathbf{k}} \Phi_{\mathbf{k}} d\mathbf{k}.$$

But use of the standard theorems for the manipulation of $\nabla_{\mathbf{k}}$ separates this into a "surface" integral, which vanishes because $\Phi_{\mathbf{k}}$ is certainly zero for sufficiently large \mathbf{k} , and other integrals which also vanish because they involve $(\mathbf{v}_{\mathbf{k}} \wedge \mathbf{H}) \cdot \mathbf{v}_{\mathbf{k}}$ and $\nabla_{\mathbf{k}} \wedge \mathbf{v}_{\mathbf{k}}$. In fact, we find that (56) is identically zero: *there is no explicit contribution from magnetic scattering to the production of entropy.*

Now we apply the variational principle in the general thermodynamic form II, taking $\Phi_{\mathbf{k}}$ as a generalized current. Since $M(\mathbf{H})$ does not contribute to the entropy production, its effect cannot be felt in the calculation and it might as well never have been present. That is, we should find for the steady state not the solution of the Boltzmann equation (54) but *the solution of the equation without magnetic terms at all.* It is well known, of course, that the magnetic terms do have an effect, modifying the solution and hence altering the transport coefficients. Yet application of a general, well-established theorem of thermodynamics (or, at least, one whose truth has not been challenged for 20 years) seems to lead to a contradictory result.

For those familiar with the thermodynamics of irreversible processes, the fact that there should be difficulties in the case of a magnetic field will come as no surprise. It is well known, for example (de Groot 1951), that the Onsager relations (28) must then be modified to read

$$(57) \quad L_{kk'}(\mathbf{H}) = L_{k'k}(-\mathbf{H})$$

showing that the coefficients are not symmetric, but are only made to agree by reversal of the magnetic field. A similar situation holds where there are Coriolis forces.

We have taken some trouble in §4 to show that Boltzmann's equation may be interpreted into thermodynamic language, and that it is consistent with the grammar of that language. Now in place of (27) we write

$$(58) \quad X_k = \sum_{k'} L_{kk'}(\mathbf{H}) \cdot J_{k'} \\ = \sum_{k'} \{ L_{kk'}^0 + M_{kk'}(\mathbf{H}) \} \cdot J_{k'}$$

where $L_{kk'}^0$ represents the scattering operator without magnetic terms and $M_{kk'}(\mathbf{H})$ is a matrix representation of the magnetic collision operator, $M(\mathbf{H})$. From the vanishing of the entropy production for magnetic scattering (which we may write $\sum_{kk'} J_k M_{kk'}(\mathbf{H}) J_{k'}$), we find

$$\begin{aligned} M_{kk'}(\mathbf{H}) &= -M_{k'k}(\mathbf{H}) \\ (59) \qquad &= M_{k'k}(-\mathbf{H}) \end{aligned}$$

since $M(\mathbf{H})$ is linear in \mathbf{H} . Thus, the coefficients $L_{kk'}(\mathbf{H})$ in (58) satisfy the proper Onsager relations, (57), in the presence of a magnetic field. The Boltzmann equation is thus represented quite consistently by (58), and the thermodynamic language is intelligible.

But the paradox concerning the application of the general variational principle is still unresolved. Indeed, the rot has spread, since the lack of symmetry of the transport coefficients in the magnetic field leads to failure of Prigogine's theorem also. The antisymmetric parts (cf. (59)) of the coefficients $L_{kk'}(\mathbf{H})$ do not contribute explicitly to entropy production, and disappear from the calculation at the first step, although they will necessarily be required at the end in the equations defining the steady state. This point seems to have been overlooked in the usual treatments.

Let us look at the problem from another aspect. Does there exist any function which can be used to fix the final state by a variational principle? We return to a purely mathematical treatment; mention of the antisymmetry of the matrix $M_{kk'}(\mathbf{H})$ suggests an answer. In proving the original theorem, I, we have used explicitly the fact that the operator L is real and symmetric (more technically, self-adjoint). But the eigenvalue theory of real symmetric matrices can be generalized to include complex matrices if these have Hermitian symmetry, i.e. if

$$(60) \qquad L_{kk'} = L_{k'k}^*$$

where $L_{k'k}^*$ means "the complex conjugate of $L_{k'k}$ ". The possibility of talking about antisymmetric matrices has thus been allowed, since this is the property of the imaginary part of the Hermitian matrix $L_{kk'}$.

The connection between the eigenvalue theory and the variational principle is very close. It is easy to prove that equations of the type

$$(61) \qquad X_k = \sum_{k'} L_{kk'} J_{k'},$$

where $L_{kk'}$ is a complex Hermitian matrix and the variables J_k may be complex, can be derived from variation of the Hermitian form

$$(62) \qquad \sum_{kk'} J_k^* \cdot L_{kk'} \cdot J_{k'},$$

subject to suitable subsidiary conditions.

To exploit this analogy, we need something equivalent to complex conjugation. In (60) this has the effect of reversing the sign of the antisymmetric part of the operator $L_{kk'}$. The corresponding effect in (59) is achieved by reversing the direction of the magnetic field \mathbf{H} . We propose the notation

$$(63) \qquad M^*(\mathbf{H}) = M(-\mathbf{H});$$

the conjugate of the operator M is the same operator with the magnetic field reversed in direction. In the same way, we may define a distribution function $\Phi_{\mathbf{k}}^*$ which is a solution of the conjugate equation, i.e. of the Boltzmann equation

$$(64) \quad X_{\mathbf{k}} = \int L(\mathbf{k}, \mathbf{k}') \Phi_{\mathbf{k}'}^* d\mathbf{k}' - M(\mathbf{H}) \Phi_{\mathbf{k}}^*.$$

With this notation, it is easy to construct a general variational principle. In effect, we find that *the general argument leading to the principal I is maintained intact if we adopt the convention that, in the presence of a magnetic field,*

$$(65) \quad \langle \Phi, \Psi \rangle \equiv \int \Phi^*(k) \Psi(k) dk.$$

Detailed derivation of this result, and its application to problems of magneto-resistance, etc., will be given elsewhere. One can, for example, write down conditions that a linear combination of trial functions should be the best approximation to the solution. It turns out that these are just the conditions proposed by Kohler (1949b) without formal proof. Here we have a theorem which guarantees their status, and shows, for example, that the corresponding estimates of resistivity must be greater than, or equal to, the true resistivity.

The most interesting question still remains: What now is the relation between the variational principle and the thermodynamic formulation II? We have seen that the unmodified thermodynamic principle does not lead to the correct answer. However, the new variational function,

$$(66) \quad \langle \Psi, L\Psi \rangle = \int \Psi_{\mathbf{k}}^* \{L_0 + M(H)\} \Psi_{\mathbf{k}} d\mathbf{k},$$

has still some meaning, in that, when $\Psi = \Phi$ and we are talking of the steady state distribution, (66) equals the actual production of entropy by collisions. In general, (66) is a function of the state of the system differing from the entropy production in that state, but the two functions become the same in the steady state. The effect of the magnetic terms is felt in fixing the steady state, but once that is reached these terms do not contribute explicitly to the production of entropy.

An alternative and, in my opinion, more fruitful convention is to suppose that the thermodynamic principle, II, is always true, in the general form in which we have stated it, and to modify the formula for the entropy production so that it always equals the variational function. That is, in place of (20) we write

$$(67) \quad \frac{dS}{dt} = -\frac{1}{T} \int \Phi_{\mathbf{k}}^* \cdot \frac{\partial f_{\mathbf{k}}}{\partial t} d\mathbf{k},$$

which might be supposed to arise from some generalized formula for the entropy, in place of (18). (It is easy to find such a formula, but it is not unique and we shall not discuss it here.)

This assumption is not so radical as one might at first suppose. Entropy is only properly defined in the equilibrium state, and it is only tentatively that

one extends the definition to non-equilibrium assemblies. We have seen that the two definitions coincide in the steady state; it is when the distributions are varying with time in a magnetic field that we find a difference, and this is a situation for which the old statistical arguments are certainly not adapted.

The failure of Prigogine's theorem is particularly interesting, because there we employ only macroscopic variables. But the same device, of postulating a conjugate current and then of writing (62) for the entropy production, works there also. Another case where something similar seems to be necessary occurs when we consider the effects of boundaries or inhomogeneities in the medium. This problem is being studied by Mr. S. Simons at the Cavendish Laboratory.

The heart of the matter seems to be the failure of the principle of microscopic reversibility in the presence of a magnetic field. In order to retrace the motion, we must not only reverse velocities but also the directions of all magnetic fields. If there were an argument giving an unambiguous combinatorial definition of entropy in non-stationary states, might it not depend on the conditions for time reversal?

Setting aside this very deep question, the difficulty at the moment seems to be in giving a clear meaning to Φ_k^* , which is the conjugate to a distribution function. The best we can do seems to be as follows: Suppose that Φ_k is an arbitrary distribution in the given magnetic field. One could imagine a set of forces for which Φ_k is actually the steady state solution. Then Φ_k^* is the steady state distribution with those same electric fields, etc., but with the magnetic field reversed. This is clumsy, but at least has "physical" significance.

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DISCUSSION OF ZIMAN'S PAPER

There was no time for detailed discussion, but **Prigogine** gave notice that he doubted the validity of part of Ziman's thermodynamic interpretation. **Ziman** agreed that further discussion on this point would be useful.

A GENERAL EXPRESSION FOR THE CONDUCTIVITY TENSOR¹

By R. KUBO²

In connection with the papers of Professor Prigogine and Dr. Ziman and also with the remark made by Professor Bardeen, I would like to discuss briefly a general expression for the conductivity tensor. Without referring to the Boltzmann-Bloch equation, which is a certain approximation valid only under a rather restricted condition (as was discussed by Professor Prigogine), we can write down an exact formula for the electrical conductivity. Let us denote the Hamiltonian of a system by H . This includes everything in the absence of the field: the kinetic energy, potential energy of the electrons and of the lattice atoms, interaction between electrons and lattice, and so on. But the interaction of the system with the applied electric field, which we call H_{ex} , is not included in H . The conductivity tensor for an oscillating electric field can be expressed in the form

$$[1] \quad \sigma_{\mu\nu}(\omega) = \int_0^\beta \int_0^\infty \{ \text{Tr } \rho_0 \} j_\nu(0) j_\mu(t + i\hbar\lambda) e^{-\omega t} dt d\lambda,$$

where ρ_0 is the density matrix representing the equilibrium distribution of the system in absence of the electric field:

$$\rho_0 = e^{-\beta H} / \text{Tr} \{ e^{-\beta H} \},$$

β being equal to $1/kT$. j_ν and j_μ are the current operators of the whole system in the ν and μ directions respectively, and $j_\mu(t)$ gives the natural motion of the current as determined by the Hamiltonian H ; thus

$$j_\mu(t) = \exp(iHt/\hbar) j_\mu \exp(-iHt/\hbar).$$

Eq. [1] is derived by a simple perturbation calculation. We assume that at $t = -\infty$ the system was in the equilibrium represented by ρ_0 . A sinusoidal electric field was switched on at $t = -\infty$, which however is assumed to be sufficiently weak. From the equation of motion

$$i\hbar \dot{\rho} = [H + H_{ex}(t), \rho]$$

we can easily obtain the change of ρ to the first order of H_{ex} :

$$\rho - \rho_0 = \frac{1}{i\hbar} \int_{-\infty}^t \exp(-Ht'/i\hbar) [H_{ex}(t'), \rho_0] \exp(iHt'/i\hbar) dt' + O(H_{ex}^2).$$

Therefore the current is given by

$$[2] \quad \overline{j_\mu(t)} = \frac{1}{i\hbar} \int_{-\infty}^t \{ \text{Tr} [H_{ex}(t'), \rho_0] \} j_\mu(-t') dt'$$

where $H_{ex}(t')$ will be replaced by $-e\chi E(t')$, $e\chi$ being the total dipole moment of the system. Using the relation

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$$[A, e^{-\beta H}] = \frac{\hbar}{i} e^{-\beta H} \int_0^{\beta} e^{\lambda H} \dot{A} e^{-\lambda H} d\lambda,$$

Eq. [2] is transformed into Eq. [1]. Either Eq. [1] or [2] can be used, but Eq. [1] is more symmetrical.

This formulation was actively discussed last year in Japan. First Nakano (1) discussed a particular case of Eq. [1] as an application of the method used by Kubo and Tomita in their general theory of the magnetic resonance problem. It was further discussed by several people including myself (3). Professor Feynman also discussed the same problem while he was visiting Japan last summer. I was informed that it was discussed in the United States by Lax, Luttinger, Kohn, and maybe by some others. I would like to discuss here briefly the implications of this sort of expression, which is quite general but admittedly quite abstract.

(1) We know, for example, that the Debye formula for the magnetic susceptibility is generalized to

$$\chi = \langle M^2 \rangle / kT,$$

where M is the magnetic moment of the whole system. This equation can be further generalized to the non-equilibrium case (2) in which the complex susceptibility can be expressed generally in terms of spontaneous fluctuation of the magnetization of the system. This is to show that our formula is to be regarded as a straightforward extension of the familiar formulae of susceptibility (response in general) to non-equilibrium situations. Such an extension is always possible so long as we confine ourselves to "linear dissipative" systems.

(2) It can be easily seen that Eq. [1] or [2] is actually equivalent to the well-known Heisenberg-Kramers dispersion formula plus the familiar expression of absorption given by the usual application of time-dependent perturbation, provided that one allows the use of the integral expression of delta (plus or minus) functions. We must admit a certain mathematical difficulty for the convergence of the integral, but any convergence factor which may be introduced is enough to give the right answer. Physically, we have to exclude the long Poincaré cycle. This is essentially the very difficult question as to how irreversibility arises from reversible motion; but we shall not discuss this here.

(3) The correlation of the spontaneous currents may be defined by

$$\Psi_{\mu\nu}(t) = \langle \{j_\nu(0)j_\mu(t)\} \rangle = \langle \{j_\nu(\tau)j_\mu(t+\tau)\} \rangle.$$

The average sign means the average over the density matrix ρ_0 . The conductivity can be also written in terms of these correlation functions. For example,

$$[3] \quad \text{Re } \sigma_{\mu\nu}^s(\omega) = \frac{1}{E_\theta(\omega)} \int_0^\infty \Psi_{\mu\nu}^s(t) \cos \omega t dt,$$

where the superscript s means the symmetric part of the tensor, and $E_\theta(\omega)$ is the average energy of an oscillator with the frequency ω at the temperature $T = 1/k\beta$. Eq. [3] is the so-called fluctuation-dissipation theorem, a particular case of which is the well-known Nyquist theorem for the thermal noise in a

resistive circuit. Derivation of [3] by our argument is equivalent to that of Callen and Welton (4). We can further show that the fluctuation-dissipation theorem applies also to $\text{Im } \sigma_{\mu\nu}^a(\omega)$ (antisymmetric part), but the other parts of the tensor, $\text{Im } \sigma_{\mu\nu}^s(\omega)$ and $\text{Re } \sigma_{\mu\nu}^a(\omega)$, are more complicated. They can also be written in terms of correlation functions, but it is not so simple.

(4) This is related to the following fact. In the classical case, we can show that the correlation functions defined above are related to the relaxation functions in a simple manner. The relaxation function $\Phi_{\mu\nu}(t)$ means the decay of the current $j_\mu(t)$ when an electric field of unit strength is applied in the ν -direction from $t = -\infty$ up to $t = 0$. The classical relation is simply

$$\Phi_{\mu\nu}(t) = \Psi_{\mu\nu}(t)/kT.$$

In quantum mechanical systems we have instead

$$\Phi_{\mu\nu}(t) = \int_{-\infty}^{\infty} \frac{2}{\hbar\pi} \log \coth \frac{\pi}{2\beta\hbar} |t-t'| \cdot \Psi_{\mu\nu}(t') dt'.$$

This complication for the quantum mechanical system should be noticed.

(5) The Onsager relations can easily be obtained from [1]:

$$\sigma_{\mu\nu}^s(\omega, |H|) = \sigma_{\mu\nu}^s(\omega, -|H|),$$

$$\sigma_{\mu\nu}^a(\omega, |H|) = -\sigma_{\mu\nu}^a(\omega, -|H|),$$

$$\text{Re } \sigma_{\mu\nu}(\omega, |H|) = \text{Re } \sigma_{\mu\nu}(-\omega, |H|),$$

$$\text{Im } \sigma_{\mu\nu}(\omega, |H|) = -\text{Im } \sigma_{\mu\nu}(-\omega, |H|),$$

where H is the magnetic field.

(6) For the static case ($\omega = 0$), Eq. [3] goes into

$$\sigma_{\mu\nu}^s = \frac{1}{2kT} \int_{-\infty}^{\infty} \Psi_{\mu\nu}^s(t) \cos \omega t dt.$$

It may be worth while to notice that this is a generalized form of Einstein's relation connecting the mobility to the diffusion constant. For some simple cases, one can easily obtain Einstein's relation from this formula. This consideration is often very useful.

(7) We must admit that Eq. [1] or [2] does not solve the problem of calculating the conductivity for a given system, unless one has the prescription how to handle it. The method of calculation, moreover, depends on the situation. First of all, we can show that the usual Bloch equation is related to this general formula. When one applies the damping theory technique with a certain perturbation term in H one can easily go back to the Bloch equation as an approximation, which may of course be sufficient in the circumstances. For metallic conduction, the well-known Grüneisen formula is directly derived from Eq. [1] if one assumes that the integrand decays in time as a simple exponential. It is sometimes essential to go beyond the Bloch equation, and here the general equation can give us the starting point; the approximation needed depends on the physical situation. We tried to apply the method to

conduction in a strong magnetic field where the quantization effect becomes serious. This study will be reported elsewhere.

(8) Similar expressions can be derived for other kinds of transport quantities such as heat conductivity and thermoelectric power. There is a certain difficulty which I have not yet completely cleared up as to the quantum mechanical representation of the presence of gradients of temperature or chemical potential. But I believe that our final answers are right; these give expressions involving the energy currents instead of mass currents.

(9) I do not know whether it is possible for there to exist a variational theorem for the expression [1]. We already know the existence of variational theorems for the partition function and also for the Bloch equation, but if a variational principle could be found giving equation [1] it would be more profound and more widely applicable than the known ones.

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A VARIATIONAL PRINCIPLE FOR CONDUCTION PHENOMENA IN THE PRESENCE OF A MAGNETIC FIELD OR ASYMMETRIC SCATTERING MECHANISMS¹

BY ALFRED SEEGER²

During studies of the influence of imperfections on the electrical conductivity of metals a need was felt for developing a variational principle applicable to the treatment of magnetoresistivity and of asymmetric scatterers. The presence of a magnetic field is known to destroy the symmetry requirements for Kohler's variational principle. Since the influence on the conductivity of metals of more complicated imperfections, e.g. dislocations, can usually only be calculated by an iteration procedure it suffices for many practical purposes to take account of the magnetic field by iteration. H. Bross has given a variational principle based on these ideas, which we will outline in the following.

If $\chi(\mathbf{k})$ measures the deviation of the distribution function f from its equilibrium value f_0 according to

$$(1) \quad f = f_0 - \chi(\mathbf{k}) \frac{\partial f_0}{\partial \epsilon}$$

(ϵ = energy of electron), Boltzmann's equation may be written in the form

$$(2) \quad \Lambda_I \{ \chi \} + \Lambda_{II} \{ \chi \} = 0,$$

where Λ_I is a symmetric operator and does not contain the magnetic field, whereas Λ_{II} is an asymmetric operator and may contain the magnetic field or other asymmetric scattering mechanisms.

In this context symmetry and asymmetry mean

$$(3) \quad \begin{aligned} (F, G)_I &\equiv \frac{1}{4\pi^3} \int F(\mathbf{k}) \Lambda_I \{ G(\mathbf{k}) \} d\tau_{\mathbf{k}} \\ &= \frac{1}{4\pi^3} \int G(\mathbf{k}) \Lambda_I \{ F(\mathbf{k}) \} d\tau_{\mathbf{k}} \equiv (G, F)_I, \end{aligned}$$

and

$$(4) \quad \begin{aligned} (F, G)_{II} &\equiv \frac{1}{4\pi^3} \int F(\mathbf{k}) \Lambda_{II} \{ G(\mathbf{k}) \} d\tau_{\mathbf{k}} \\ &\neq \frac{1}{4\pi^3} \int G(\mathbf{k}) \Lambda_{II} \{ F(\mathbf{k}) \} d\tau_{\mathbf{k}} \equiv (G, F)_{II}. \end{aligned}$$

When Λ_{II} contains the effects of the magnetic field only and no additional effects (due, say, to static imperfections), it is antisymmetric, i.e.

$$(4a) \quad (F, G)_{II} = - (G, F)_{II}.$$

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An example of a static scatterer which gives rise to both symmetric and antisymmetric scattering is a screw dislocation in a metal (see Seeger and Stehle 1956).

We now assume Λ_{II} to be small compared with Λ_I .

We put

$$(5) \quad \Lambda_{II} = \lambda \Lambda_{II}'$$

where Λ_{II}' is of the same order of magnitude as Λ_I .

We put further

$$(5a) \quad \chi = \sum_{r=0}^{\infty} \lambda^r \chi^{(r)}.$$

Equation (2) may then be transformed as follows:

$$(6a) \quad \Lambda_I \left\{ \sum_{r=0}^{\infty} \lambda^r \chi^{(r)} \right\} + \lambda \Lambda_{II}' \left\{ \sum_{r=0}^{\infty} \lambda^r \chi^{(r)} \right\} = 0,$$

$$(6b) \quad \sum_{r=0}^{\infty} [\lambda^r \Lambda_I \{ \chi^{(r)} \} + \lambda^{(r+1)} \Lambda_{II}' \{ \chi^{(r)} \}] = 0,$$

$$(6c) \quad \sum_{r=0}^{\infty} \lambda^r [\Lambda_I \{ \chi^{(r)} \} + \Lambda_{II}' \{ \chi^{(r-1)} \}] = 0.$$

Since λ is arbitrary, we have

$$(7a) \quad \Lambda_I \{ \chi^{(0)} \} = 0,$$

$$(7b) \quad \Lambda_I \{ \chi^{(r)} \} + \Lambda_{II}' \{ \chi^{(r-1)} \} = 0, \quad r \geq 1.$$

Eq. (7a) may be solved by Kohler's variational principle. We therefore restrict ourselves to the discussion of Eq. (7b). We start from

$$(8a) \quad (F, G)_I = (G, F)_I$$

and

$$(8b) \quad (F, F)_I \geq 0.$$

Conditions (8) must be verified for the particular scattering mechanism involved. They are satisfied for thermal scattering (see, e.g., Jones 1956).

We consider now

$$(9) \quad (\chi^{(r)} - \psi^{(r)}, \chi^{(r)} - \psi^{(r)})_I \geq 0$$

or

$$(9a) \quad (\chi^{(r)}, \chi^{(r)})_I - 2(\chi^{(r)}, \psi^{(r)})_I + (\psi^{(r)}, \psi^{(r)})_I \geq 0$$

and suppose that $\psi^{(r)}$ satisfies the equation

$$(10a) \quad (\psi^{(r)}, \psi^{(r)})_I = -\frac{1}{4\pi^3} \int \psi^{(r)} \Lambda_{II}' \chi^{(r-1)} d\tau_k$$

or, by applying Eq. (7b),

$$(10b) \quad (\psi^{(r)}, \psi^{(r)})_I = (\psi^{(r)}, \chi^{(r)})_I.$$

Inserting Eq. (10b) into Eq. (9a) gives us

$$(11) \quad (\psi^{(r)}, \psi^{(r)})_I \leq (\chi^{(r)}, \chi^{(r)})_I.$$

Eq. (11) shows that the correct solution $\chi^{(r)}$ of Eq. (7b) is that function $\psi^{(r)}$ which satisfies the auxiliary condition (10a) and makes $(\psi^{(r)}, \psi^{(r)})_1$ a maximum. By using this variational principle the set of functions $\chi^{(r)}$ may be calculated successively. Although the formulation of this variational principle is less elegant than that given by Ziman in this conference, it is thought that it will prove to be useful in practical calculations.

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REMARKS ON THE ANOMALOUS BEHAVIOR OF ALLOYS CONTAINING TRACES OF MANGANESE OR SIMILAR ELEMENTS¹

BY C. J. GORTER,² G. J. VAN DEN BERG, AND J. DE NOBEL

ABSTRACT

The anomalous behavior of alloys containing traces of manganese and similar elements is rapidly reviewed as to electrical conductivity, magnetoresistance, susceptibility, magnetic resonances, thermoelectricity, specific heat, thermal conductivity, and Hall effect. Special reference is given to recent data obtained in Leyden. It is argued that, while the rapid decrease of the resistance sometimes occurring at very low temperatures apparently must be attributed to some kind of antiferromagnetic alignment, the resistance minimum, as well as the anomalies in thermoelectricity and the Hall effect, might be due to gaps at the crystalline boundaries.

So far anomalous behavior of alloys containing traces of manganese or other magnetic elements has been observed for a number of properties. We shall rapidly review them, giving particular reference to recent Leyden results.

A. Electrical conductivity.—Gerritsen and Linde (1) have collected many data on the electrical resistivity, finding that in several alloys it has not only a minimum but, at a somewhat lower temperature, also a maximum. This applies to Cu with Mn, Ag with Mn, and Au with Mn, Cr, Co, and Fe. At very low concentrations c (of the order of 0.1%) the temperature of the maximum increases with c , while at higher concentration both the maximum and the minimum flatten out and disappear.

B. Magnetoresistance.—In the region of temperatures and concentrations where both a maximum and a minimum occur the resistance is, according to Gerritsen and Linde, considerably decreased by a transverse or longitudinal magnetic field. At low fields H the decrease is proportional to H^2 , while at low concentrations but not too low temperatures it is, for Mn alloys, approximately proportional to $B_5^2(\mu_0 H/kT)$ where B_5 is the Brillouin function for $J = 5/2$ and μ_0 is the Bohr magneton. B_5 is proportional to the magnetization to be expected for free Mn^{++} -ions. At the lowest temperatures and at somewhat higher concentrations the decrease is not proportional to B_5^2 but smaller and less rapidly saturated.

C. Magnetic susceptibility.—Researches carried out in Strassbourg and in Stockholm (2) have shown that above liquid air temperatures the magnetic susceptibility of silver, copper, and gold containing small amounts of manganese follows Curie's law with the Curie constant to be expected from free Mn^{++} -ions. At higher concentrations the susceptibility per Mn^{++} -ion is decreased somewhat leading to antiferromagnetism at the lower temperatures. In MnAu a sharp Néel point of 500° K. is observed, while in MnAu₃ there is apparently a Néel point in the neighborhood of 120° K.

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Early unpublished Leyden data of H. M. Gijsman on a few AgMn alloys led to Curie's law at relatively high temperatures and to almost constant susceptibilities at the lowest temperatures.

Extensive partially unpublished data obtained in Schenectady (3) and Berkeley (3) indicate a maximum in the susceptibility as a function of temperature not far from the maximum of the resistivity, the temperature of which also rises with rising concentration c . In some cases the susceptibility at temperatures above the temperature of the maximum is higher than expected from free Mn^{++} -ions, while below that temperature small hysteresis effects and thermomagnetic resonance are observed. Apparently some kind of antiferromagnetic alignment occurs below a rather well defined Néel temperature. The occurrence of interaction of ferromagnetic sign between atoms at larger distance leading to an increased susceptibility above the Néel temperature is not uncommon. The hysteresis effects and the thermomagnetic remanence occur frequently in antiferromagnetics but could as well be attributed to small ferromagnetic domains.

D. Magnetic resonances.—Important data have been obtained in Berkeley (4) on Mn spin resonance and on Cu-nuclear resonance. The Mn spin resonance is anomalous below the apparent Néel temperature in the sense to be expected for antiferromagnetism. The Cu-nuclear resonance, which has also been investigated by W. van der Lugt and N. J. Poulis in Leyden, shows a slightly decreased Knight shift and rather narrow lines.

E. Thermoelectricity.—The anomalous thermoelectric power in diluted alloys, discovered in Stockholm and Leyden and recently studied in detail in Ottawa (5), seems to be a rather general phenomenon and is not confined to impurities of manganese and other magnetic elements.

F. Specific heat.—Provisional data on a Ag-Mn alloy containing 0.09% Mn obtained by J. de Nobel and R. Hartmans indicate a large extra specific heat having its maximum at a temperature between 1.5° and 2° K., which is somewhat lower than the value of the maximum resistance at about 2.2° K. At higher temperatures the magnitude of the tail in the specific heat corresponds to an internal field of about 8000 Oe. which is at least 20 times larger than that to be expected for magnetic interaction between the Mn-ions in a solid solution.

G. Thermal conductivity.—M. S. R. Chari and J. de Nobel have carried out investigations on the thermal conductivity of a number of Ag-Mn alloys and, for comparison, of an Ag-In alloy. Though an apparent anomaly was observed in the liquid helium region no essential difference was found with respect to the Ag-In alloy. However, a considerable decrease of the thermal resistance was observed in the Ag-Mn alloys in transverse magnetic fields. This decrease is not very different from the corresponding decrease of the electrical resistance and has roughly the same dependence on T and H .

H. Hall effect.—B. Franken has recently observed an increase of a few per cent in the Hall coefficient of Ag-Mn alloys in the temperature region of liquid hydrogen and liquid helium. The Hall coefficient was not dependent on

the value of the field. A similar increase was observed by Fukuroi and Ikeda (6) in a sample of impure gold, which increase has the same relative value as the rise in resistance of the sample.

DISCUSSION

It cannot be denied that in the alloys concerned a sort of antiferromagnetism occurs below a rather well defined temperature limit which shifts downward as the concentration is decreased. In view of the steep fall of the resistance observed by Linde and Giansoldati (7) below the Néel temperatures of AuMn and Au₂Mn, one might ascribe the rather steep fall of the resistance of the diluted alloys to the same cause, probably a phase correlation between the electron scattering by different Mn⁺⁺-ions; but also other explanations are feasible. This is only an effect of a few per cent at most. A much stronger effect certainly due to different scattering of oppositely spinning electrons apparently occurs when the Mn spins are all polarized in the same direction by a large external field, which leads to a decrease of the electrical resistance and of the thermal resistance up to 30%.

If this view is accepted, one would have to abandon the model of Korringa and Gerritsen, which lays a close connection between maximum and minimum of the resistivity, ascribing them as a consequence of resonance scattering. The small increase of the Hall coefficient when the temperature decreases, which seems to go parallel with the increase of electrical resistivity and which seems to be produced by magnetic as well as by non-magnetic impurities, might be attributed to a decrease of the effective number of free electrons.

A promising alternative, however, would be to attribute it to the grain boundaries, to which already attention has often been attracted (8). Because of the impurity atoms precipitating themselves at the grain boundaries, these might obtain the character of gaps presenting larger potential barriers for the electrons when the impurity content increases. These barriers might present an insulating or semiconductive behavior, and crossing them might become more difficult at lower temperatures; in this way the increase of both the resistivity and the Hall effect might be explained. There would be some analogy with the rise of the resistivity of thin films upon lowering the temperature studied by van Itterbeek, Vodar, and others (9). In the case of those thin films a pronounced dependence of the resistance on the current is observed. In this respect one may recall the early researches of G. J. van den Berg and W. J. de Haas (10) on impure gold, in which the occurrence of a small, perhaps spurious, current dependence was mentioned. The gaps might give rise to large anomalies in the thermoelectric power but not in the Peltier effect, thus leading to an over-all violation of the Kelvin relations. We realize that these suggestions have merely a provisional and speculative character.

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DISCUSSION

For discussion of this paper, see page 1291.

MAGNETIZATION AND MAGNETORESISTANCE OF SOME DILUTE ALLOYS OF Mn IN Cu¹

By R. W. SCHMITT² AND I. S. JACOBS²

We have recently been measuring the magnetization and magnetoresistance of some dilute alloys of Mn in Cu. The results we have already obtained will amplify and extend Professor Gorter's review of the anomalous magnetic and magnetoresistive behavior of these alloys. In Fig. 1 is shown the resis-

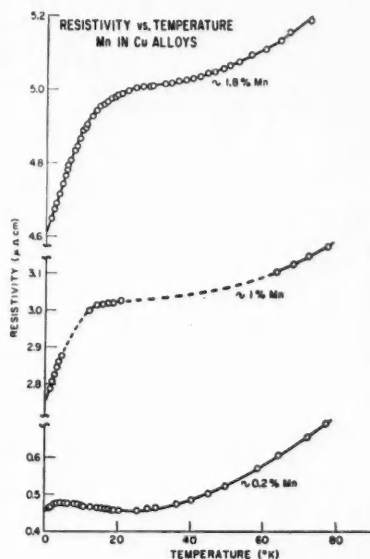


FIG. 1.

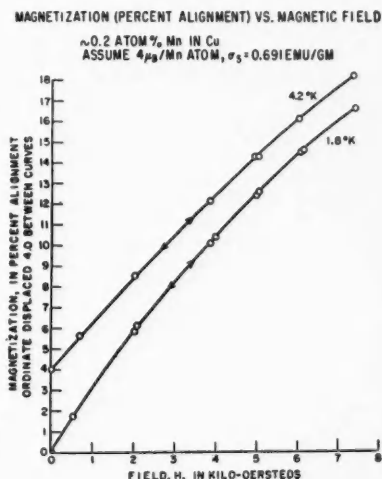


FIG. 2.

tance vs. temperature of the three alloys we have examined. Only the 0.2 atomic per cent (nominal) Mn in Cu alloy shows a definite resistance maximum but the other two alloys of higher Mn content still show an anomalous decrease in resistivity as the temperature is lowered. This behavior agrees with that found by Gerritsen and Linde (2).

The magnetic behavior of the 0.2 at. % alloy is shown in Fig. 2, where the magnetization is plotted as a function of field up to a field of ~ 7.3 kilo-oersteds. There is a marked deviation of the magnetization from linear dependence on the magnetic field for magnetizations representing as little as 10% alignment of the Mn ions. No such deviations would be expected in a

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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simple paramagnetic material for less than about 50% alignment. This deviation from linearity enables one to differentiate between the dependence of the magnetoresistance on the field and its dependence on the magnetization. In Fig. 3 is shown the magnetoresistance of ≈ 0.2 at. % Mn in Cu samples

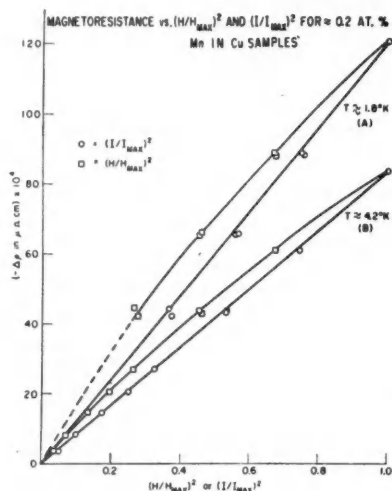


FIG. 3.

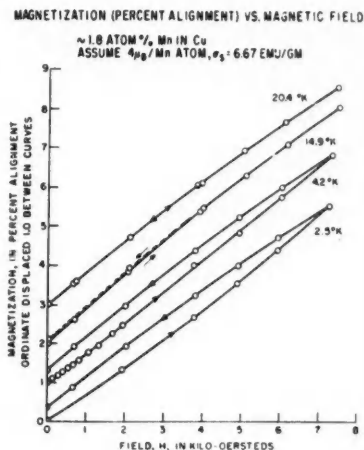


FIG. 4.

plotted as a function of the square of the field (H) and as a function of the square of the magnetization (I). The magnetoresistance appears to depend quadratically on the magnetization: $\Delta\rho = -bI^2$, where b is independent of H but is a function of the temperature.

In the alloys of higher Mn content hysteresis appears in both the magnetization and magnetoresistance. The 1 at. % (nominal) and 1.8 at. % alloys behave in a similar manner, but since we have so far examined the 1.8 at. % alloy more extensively, we shall illustrate the results with data on this alloy only. Fig. 4 shows the magnetization vs. field of the 1.8 at. % alloy as the field is increased from zero to a maximum of ~ 7.3 kilo-oersteds on the virgin sample and then decreased again to zero. Hysteresis appears in the magnetization as the temperature is decreased. Simultaneously, hysteresis appears in the magnetoresistance, as is shown in Fig. 5. Clearly, here again the magnetoresistance is not dependent only on the magnetic field but is determined by the magnetization. The relation between magnetoresistance and magnetization seems to be less simple than with the more dilute alloy. In Fig. 6 this is illustrated by data on the 1.8 at. % sample at 4.2°K . The three sets of curves represent the magnetoresistance as a function of H^2 (1), as a function of HI (2), and as a function of I^2 (3). The best fit of all the data seems to be a relation of the form $\Delta\rho = -(a + bI^2)$. The initial portions of the virgin curve must deviate from such a relation although no resistance data have yet been taken

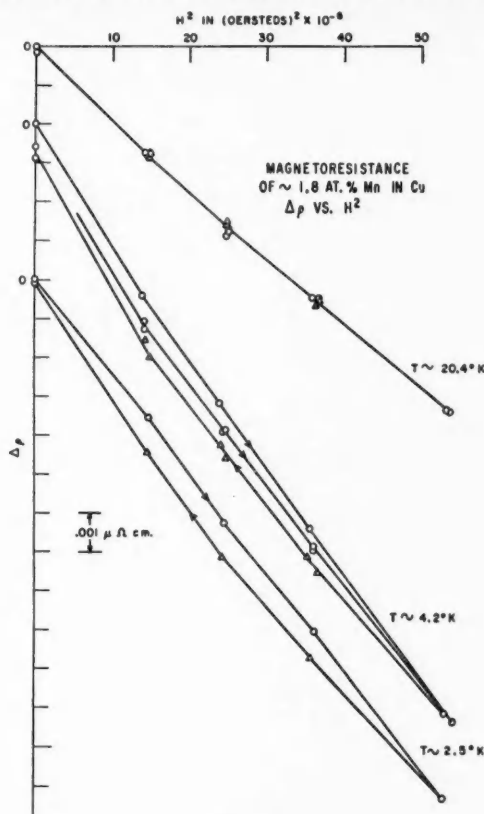


FIG. 5.

at these low fields. Curve 2 indicates that the relation $\Delta\rho = -(a+bHI)$ may be a slightly better fit to all of the data except that of the virgin curve. A more detailed analysis of the data than we have yet completed, as well as further experiments at the lowest field values, will be required.

These results indicate, quite clearly, the onset of a cooperative magnetic effect in these alloys at low temperatures. However, the behavior of the magnetoresistance is different from that observed in most ferromagnetic materials. Fig. 7 shows schematically the variation of resistance with field of a material such as nickel, at temperatures below the Curie temperature but still high enough for the intrinsic magnetization to be increased by application of sufficiently large fields. The effects at low fields arise because a domain has a higher resistance if the current flows parallel to the magnetization than if it flows transverse to the magnetization. No such orientation effect is present in the dilute alloys of Mn in Cu, where Gerritsen (1) has found the transverse

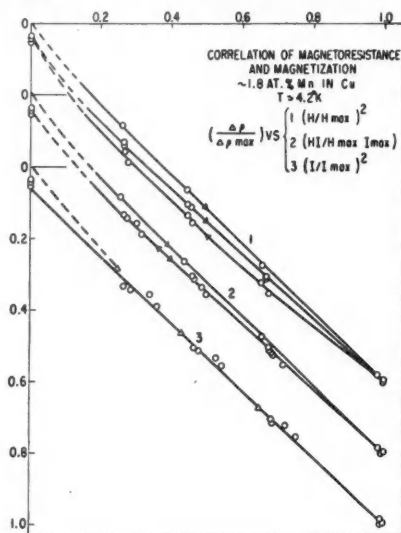


FIG. 6.

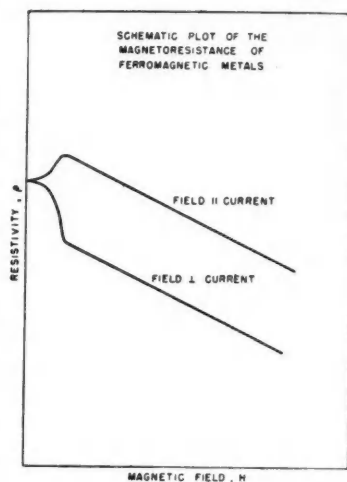


FIG. 7.

and longitudinal magnetoresistance to be approximately equal. The small differences observed are in a direction and of a magnitude that can be accounted for by the normal magnetoresistance, which increases with the square of the field and is larger in the transverse direction. In sufficiently high fields the resistance of a normal ferromagnetic metal decreases with increasing field at about the same rate for longitudinal as for transverse fields. This, too, is shown in Fig. 7. This decrease is due to the increase in intrinsic magnetization produced by the field, and presumably a similar explanation is valid for dilute alloys of Mn in Cu (3). However, in ordinary ferromagnetic metals the decrease is a linear function of the field whereas for the dilute Mn alloys the decrease is roughly a quadratic function of the field. Thus the cooperative magnetic phenomenon observed in the dilute alloys of Mn in Cu seems not to be a simple ferromagnetic one. It may be that a model suggested by J. C. Fisher can be used to develop a sufficient phenomenology. In this model the ferromagnetic interaction is viewed as dominating within small domains but the domains themselves are coupled antiferromagnetically. Professor Gorter has pointed out that if the domains are smaller than the electronic free path one would expect the magnetoresistance to be proportional to the square of the measured magnetization of the samples, as we have observed in the most dilute alloy. However, the phenomenology of such a model must be worked out more carefully and its results compared quantitatively with the results here presented.

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DISCUSSION

For discussion of this paper, see page 1291.

ON THE RESISTIVITY ANOMALIES IN SOME DILUTED ALLOYS¹

By J. KORRINGA²

The newer experiments on diluted alloys of Mn in Cu, which were reported at this conference by Gorter and by Schmitt, have confirmed some of the ideas that have been suggested earlier (1), but have done little to strengthen the belief that a simple scattering mechanism can account for all the known properties.

Measurements of the magnetoresistivity $\Delta\rho/\rho$ and the magnetization $M(H)$ on the same sample, as reported by Schmitt, show that the two are closely related, and that we have $\Delta\rho/\rho \sim M^2$. This result, which was anticipated in Ref. 1, would also be obtained in any model for which the scattering of conduction electrons is predominantly elastic, provided that (1) the cross-section for scattering of an electron by a Mn-impurity depends on the relative spin-orientation of the two, (2) there is no interference of scattered waves from different centers, and (3) the total current is the sum of the currents of the two spin orientations. The first property seems quite in line with Friedel's calculations reported at this conference: the Mn-ion would approximately have the configuration $(3d)^5 S_{5/2}$ —as is also indicated by the high temperature susceptibility—so that the wave function of the electron during scattering can have a $3d$ -part only if its spin is not parallel to that of the ion. The observed large negative values of $\Delta\rho/\rho$ ($\Delta\rho/\rho = 0.3$) would require a rather large difference between the two cross-sections (by a factor 3 or more). The second condition would be fulfilled if the Mn-ions do not form a superlattice.

A steep fall of the resistance in zero magnetic field can, in a qualitative sense, be brought into connection with the observed magnetic anomalies at low temperatures. For example, at a temperature below a magnetic transition, a scattering process in which the electron and a Mn-ion exchange a quantum of spin angular momentum would become inelastic from the point of view of the electron. The energy exchange would be $2\mu H_i$, if H_i is the effective Weiss field. For temperatures $kT \ll \mu H_i$ this becomes impossible, and this scattering process would be eliminated as a source of resistance. In view of the smallness of the observed drop (a few per cent) such an explanation seems, generally speaking, not implausible. It is, however, incompatible with the observed value of the paramagnetic resonance line width, as was pointed out by Kittel (2). The frequency of inelastic collisions, required to explain the drop in resistance, would correspond to a much shorter relaxation time than was indicated by the line width.

However, the rise in resistance with decreasing temperature for somewhat higher temperatures, observed among others for low concentrations, and

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

This report has been written at the end of the congress. The author has profited from private discussions with several participants; the outcome of these discussions has partially been included.

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leading to a resistance minimum, and, more in particular, the detailed functional dependency on T , seems to be the main stumbling block for any simple scattering theory. On the other hand, the hypothesis that the electrons at the Fermi level are subjected to a resonance scattering does not only lead to $\rho(T)$ -curves similar to the observed ones, but can also be correlated rather plausibly—for example in the manner expanded in Ref. 1—with the other properties, such as the magnetoresistivity and thermoelectric effect. I would like to remark here that the same can be said for the magnetic anomalies and, to some extent, for the Cu nuclear resonance data reported by Kittel and co-workers (2).

Here again, a source of exchange interaction between the Mn-ions can be readily found, viz. as an indirect exchange via the conduction electrons (3). Applying the calculation of such an indirect exchange given by Ruderman and Kittel (4) to the set of Mn-ions instead of the nuclei would lead one to expect an antiferromagnetic exchange at the distances found in diluted alloys. This is not conclusive, however, because even if one does not allow for anomalies of the Fermi surface, the exchange energy between a Mn-ion and a conduction electron is, as was pointed out by Bloembergen, not the same for all electronic states. But, as was remarked by Kittel (2), a ferromagnetic exchange by this mechanism would lead to a strong electron spin polarization, i.e. a large Knight shift, contrary to the observations, whereas an antiferromagnetic exchange probably would be accompanied by a much larger nuclear spin resonance line broadening than is observed. Here again, the resonance hypothesis might offer a way out of these difficulties. In fact, the magnetic interaction between an electron in the fractional "local state" introduced in (1) and the Mn-ion can be considered as a model for the source of the Weiss field H_0 (energy $\mu H_0 = \epsilon_1$ of Ref. 1). With all the limitations of this model it seems that a given Weiss field could then be obtained with a much smaller electron-spin polarization, i.e. with much smaller nuclear resonance line broadening. (This model leads to an antiferromagnetic exchange.)

Apart from a fundamental approach to the problem, a further phenomenological analysis of the experimental results, in particular also of the specific heat data, seems very desirable.

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DISCUSSION OF THE PAPERS OF GORTER, VAN DEN BERG, AND DE NOBEL; SCHMITT AND JACOBS; AND KORRINGA

Aigrain: In measurements on the Hall effect in non-homogeneous samples, we have found that although the grain boundaries can provide high resistivity barriers the Hall effect itself is not affected by them. If grain boundaries were responsible for the anomalies, this would tend to suggest that there should be no anomalies in the Hall effect.

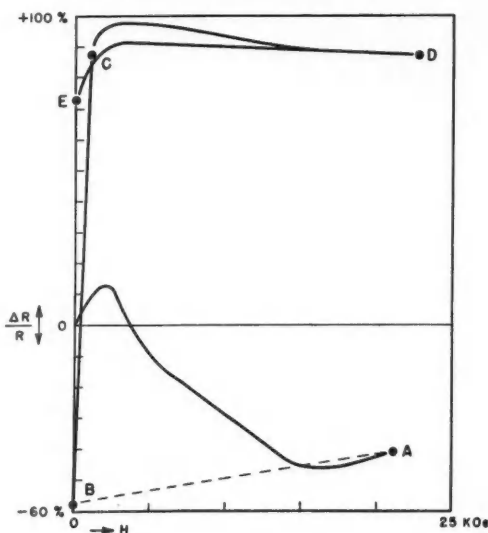
Fröhlich: Part of Gorter's discussion is not at all speculative—his deduction of a decrease in the number of free electrons at low temperatures from the Hall effect and electrical conductivity. These determine N and τ uniquely. Of course this does not explain why it should happen.

Gerritsen: If an antiferromagnetism (whether or not mixed with ferromagnetism) were responsible for the anomalies in the magnetoresistance, and boundary effects for the maximum in the temperature-resistance curves of the dilute alloys, the relation found experimentally between the two anomalous effects would not be comprehensible. A boundary effect on the resistance seems to be rather improbable, considering the linear relation between the temperature of the maximum and the concentration of the transition metal in the alloy. The argument against a boundary effect is emphasized by the evidence that the effect of the maximum is not qualitatively influenced by annealing.

Further I would like to warn against using data obtained with impure metals as an argument for a general description of the phenomena under discussion. It is known that impure gold mostly contains a certain amount of iron, so that, referring to the results on e.m.f. measurements with AgMn and impure gold, Dr. Gorter essentially has compared two dilute alloys.

Chambers: The Hall coefficient cannot be simply equated to $(Nec)^{-1}$, where N is the number of conduction electrons, unless the Fermi surface is spherical (and the scattering isotropic). Kohler suggested that for group I metals it would tend to $(Nec)^{-1}$ at high fields, but this is not confirmed experimentally.

Gerritsen: The hysteresis effects, as reported by Dr. Schmitt, are interesting. The existence of ferromagnetism and antiferromagnetism in still more dilute alloys is perhaps best illustrated by considering results obtained with



three specimens of silver manganese (containing 0.03^a, 0.05, and 0.09 at. % manganese, respectively). The results for the 0.03^a at. % sample are sketched here (A. N. Gerritsen, *Physica*, **19**, 61 (1953); *Commun. Kamerlingh Onnes Lab.*, No. 291 c; and J. Korringa and A. N. Gerritsen, *Physica*, **19**, 496 (1953); *Commun. Suppl. Kamerlingh Onnes Lab.*, No. 106). In this graph $\Delta R_H/R_0$ at 4.2° K. has been plotted against the transverse field. The measured points have been omitted in this sketch for the sake of clarity; the curves have been measured in the sequence *O-A-B-C-D-E*. When it is assumed that in these special cases there exists a spatial ordering, then, in terms of the Korringa-Gerritsen explanation, the "ferromagnetic" state is reached after increasing the field to *A*. In this situation, those electrons with a spin opposite to the spin of the electrons in the bound states of the aligned ions will not be scattered by these ions, and thus they will short-circuit the influence of the impurities on the current. This situation remains after the field is removed (*B*), but is not yet a situation of zero entropy; this will be reached when a small field is then applied (*C*). This is a situation of antiferromagnetism, in which the scattering of electron spins of each sign with the equal number of opposite ion spins is maximal.

Fiske: In CuMn we have found in experiments at General Electric that the resistance minimum is not shifted by annealing, though the total resistance is of course shifted considerably.

Mendelssohn: In experiments at Oxford some years ago (MacDonald and Mendelssohn, *Proc. Roy. Soc. A*, **202**, 523 (1950)) on moderately pure magnesium, a resistance minimum was observed which did not shift appreciably when a magnetic field was applied sufficient to double the absolute value of the resistance.

MacDonald: The chairman has suggested that I might outline some of our work here on this problem of the resistance minimum. In most of our alloys copper has been the parent, and we have made a systematic investigation of the influence of a large number of solute impurities of different valencies and atomic masses. Concurrently we have investigated the even more striking anomalies in thermoelectric power. We have not studied the alloys which show a maximum as well as a minimum, such as the alloys with manganese investigated extensively at Leyden, and so we have had to deal with a simple minimum. We find that impurities Sn, Fe, Ge, Pb, and Bi all show a minimum in Cu, while Ag, Au, and Ni do not.

Following the example set at Leyden, Dugdale and I have recently studied very dilute alloys (with between 0.01% and 0.05% atomic concentration) down to about 0.1° K. In this range we have found minima in CuFe and AuFe; while the resistance curve of the CuFe flattens fairly abruptly below 1° K., that of the AuFe is still rising with no sign of turnover at the lowest temperatures reached. No minimum was found in LiMg in this range.

Some of the tentative explanations put forward for substances behaving like CuMn obviously are not applicable to the alloys we have studied. The resonance scattering theory of Gerritsen and Korringa appears to require a

resistance maximum at a temperature of the same order of magnitude as the temperature of the minimum; in fact no maximum is observed at all in the experimental range. Again it is difficult to see the relevance of the *d*-band picture for CuSn, say, since here the *d*-bands are presumably all filled: in contrast we have no minimum in CuNi, where according to the *d*-band picture we might expect one.

We may ask how far is the parent metal specifically responsible for the anomaly. For example, I believe there is no significant evidence that an alkali metal will act as parent; though this may be because with the exception of LiMg one cannot dissolve heterovalent impurities in any of the alkali metals. Nearly all the dilute alloys in which the anomaly occurs have heterovalent solvent and solute, although AuCu (enlike CuAu) surprisingly enough appears to give the anomaly. There is good evidence for the anomaly in AuCu, although if any convincing theory should appear which strictly requires heterovalency we should be very willing to re-examine this alloy. At all events there is no anomaly in LiMg, which suggests that the parent may be important.

Ziman: How about aluminum as parent?

Pearson: Aluminum as parent shows no thermoelectric anomalies comparable with those of copper.

Mendelssohn: Boorse and Niewodniczanski (Proc. Roy. Soc. A, **153**, 463 (1935-36)) found that a previous report of a resistance minimum in aluminum could not be confirmed.

Sondheimer: You say that magnesium causes no anomaly in lithium as parent; but unless it does show one in copper as parent, this is not very good evidence for showing that the parent is important. Is this known?

Pearson: No. CuMg alloys have shown an anomaly, but since there was also an appreciable anomaly in the "pure" copper treated in the same way, this is not conclusive evidence. We are reinvestigating these alloys now.*

Gerritsen: The effects of small iron concentrations as reported by Dr. MacDonald become different when the 0.1-1 at. % region is approached. Our results have now been completed with the measurements of CuNi, AuFe, AuCo, and AuNi alloys. AuFe and AuCo show anomalies of the AuMn type in the zero field resistance temperature curve and in the magnetoresistance. It must be noted, however, that the effect in AuFe resembles more a Néel transition, like that measured in gold-manganese compounds by Linde, than a sharp maximum.

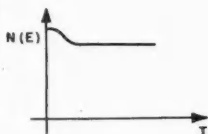
For CuNi and AuNi no maxima in the resistance-temperature curve have been found. The magnetoresistances are anomalous, which can be seen in a Kohler plot for both alloys. In the case of CuNi the resistance decreases in a magnetic field at 4.2° K. for 2.2 at. % Ni; while in the case of AuNi, only alloys containing less than 1.2 at. % have been measured, and these do not show a resistance decrease in a field. These results are to be published in *Physica*.

*These investigations subsequently showed that magnesium did not cause a resistance minimum in copper.

Mott: Superconductors are pre-eminent in showing very marked anomalies in resistance and thermoelectric power. It has been suggested that the same sort of mechanism might be responsible both for superconductivity and for the kind of anomaly we have been discussing—an interaction of the type proposed by Fröhlich and Bardeen.

Fröhlich: This is an interesting possibility. It would explain how an external magnetic field would destroy the effect and so give a negative magnetoresistance, and similarly for the internal field of a ferro- or antiferro-magnetic. In fact, work along these lines has been followed up by Bhatia.

Bhatia: The same interaction between the phonons and electrons that is thought to give rise to superconductivity can be used to derive a variation with temperature of the density of states at the Fermi level of normal metals, of the type shown in the figure:



If we had only the ideal resistance, this would not be sufficient to explain the resistive minimum. But when residual resistance is caused by the introduction of impurities, the rise in density of states with decreasing temperature causes a rise in resistance.

Pines: There is no experimental confirmation of this rise in $\rho(E)$. Measurements of the Knight shift combined with the spin lattice relaxation times show no signs of it. Odd things are found in sodium, but these go in the opposite direction.

Mott: If the interaction leading to superconductivity is at the bottom of all this, we should look for an isotope effect.

White: I should like to ask Drs. Korringa and Gorter and others for an interpretation of some recent results on the electrical resistance of pure manganese obtained by Woods and myself. These measurements were on electrolytic flake manganese of very high chemical purity, i.e. of small metallic impurity content; presumably the unannealed specimen contained quite a lot of hydrogen, as its resistance was very high and did not fall appreciably on cooling to helium temperature—a similar behavior to that noted by Meissner and Voigt. However, the vacuum annealed sample gave a resistivity of about 150×10^{-6} ohm-cm. at room temperature, falling very little down to 60° K.—except for a slight dip at about 100° K.—but then falling to about one-tenth its room temperature value at 3° K. Assuming Matthiessen's rule to be valid, the ideal resistivity varied as T^2 from helium temperatures up to about 25° K. Acknowledging the fact that α -manganese has a very complicated structure, it is difficult to see what type of electron scattering process can produce a T^2 variation in the resistance.

Schmitt: Neutron diffraction experiments on α -manganese indicate that

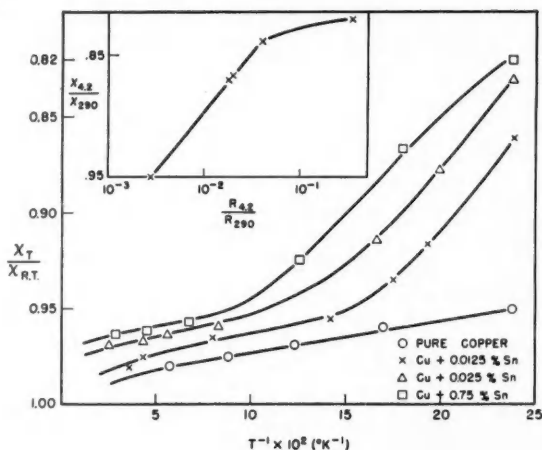
there is an antiferromagnetic transition in this temperature range. The anomaly that you find is probably related to this transition.

Borelius: We cannot be sure that the atoms of the transition metals in these dilute alloys are distributed at random. May there not be clustering?

Korringa: Many of the parameters, including the total residual resistivity, are rather closely proportional to the concentration. This would not be expected if clustering were appreciable.

MacDonald: Here in Ottawa Hedgcock has made experiments on the magnetic susceptibility of some of the dilute alloys which show a minimum but not a maximum. Here again we find anomalies at low temperatures, as Professor Gorter has already reported in the manganese alloys.

Hedgcock: Magnetic susceptibility studies made on alloys containing a non-transition element impurity (tin with $c < 1\%$) also show magnetic anomalies in the region of the resistance minimum. At low temperatures there is a paramagnetic contribution to the total susceptibility of the alloy which increases with increasing tin content (see figure). In addition to this there is a deviation from a T^{-1} plot of the susceptibility of the alloy in the region of the resistance minimum—the deviation occurring at higher temperatures as the



impurity content is increased. The inset in the figure shows the susceptibility of the alloy at 4.2° K. relative to the room temperature value, plotted as a function of residual resistance of the alloy, and it is quite apparent that there is a saturation effect occurring. The magnetic susceptibility measurements agree with the general resistive behavior in these alloys. It is hoped to continue the measurements on alloy systems with different valence impurities. A more detailed account of the measurements has been presented for publication.

MacDonald: Any possible explanation of these anomalies would seem to require a highly energy-dependent scattering cross-section. Dr. J. S. Dugdale

has therefore tried the effect of high pressure in the experiments, but he has found no very dramatic changes.

Korringa: If the source of the anomalous scattering is fundamentally tied up with the Fermi level, you would not expect pressure to cause any dramatic differences.

Mendelssohn: Have the Ottawa people looked at the thermal conductivity of their alloys?

White: Woods and I have examined copper-iron alloys which showed a marked electrical resistance minimum but we could not be sure whether the thermal parameter— $WT \equiv T/K$ —showed the same behavior required to preserve constancy in the Lorenz ratio, since the lattice conductivity complicates the picture. However, in the case of higher purity metals in which the lattice conductivity is less important—gold, copper, magnesium (see also Rosenberg; Spohr and Webber)—the product of thermal resistance and temperature did appear to show a similar minimum as might be expected.

Mendelssohn: I think it is quite important to remember that it is possible to imagine two different types of anomaly in the thermal resistance—one where as the temperature decreases the resistance first decreases below the value you would expect from the T^2 law and then rises, however always remaining below the simple theoretical value; and one in which the resistance simply starts to rise above the theoretical value as low temperatures are approached. In experiments at Oxford we found W to be lower than the T^2 law would predict.

Pines: A possible mechanism for the role which grain boundaries play in the phenomena under discussion is the clustering of the impurities along a grain boundary. Most mechanisms involving impurity atoms are sensitive to clustering. For example, the impurity state spin resonance spectrum in silicon is markedly altered when clustering takes place.

There are also two points I should like to get clear. Is the effect completely washed out at high enough concentrations? And have sufficiently dilute solutions of manganese-copper been examined to ensure that at sufficiently low concentrations the resistance drop does not disappear, leaving only a minimum in place of the minimum followed by a maximum?

Gorter: For very dilute CuMn alloys we cannot get down to sufficiently low temperatures, but it looks as if the drop always remains.

Korringa: If the experiments are analyzed according to our theory, we may derive as functions of the concentration the resonance width Δ and the energy ϵ of the resonance band above the Fermi level. When these are extrapolated to zero concentration we find $\epsilon \rightarrow 0$ while Δ remains finite. This would suggest that at sufficiently low concentrations the maximum disappears and only the minimum remains; but of course we should not claim that this extrapolation is necessarily justified.

Pearson: In copper with 0.44 atomic % iron the minimum occurs at about 26° K.; by 0.1° K. the curve has completely flattened off without as yet any sign of a drop. In the copper-iron alloys the minimum persists when magnetic fields up to 15,000 oersteds are applied; the same is also true for copper-tin.

Sondheimer: Do you get a big magnetoresistance?

Gorter: ρ increases with H in these alloys; it's quite different from those with manganese as impurity.

MacDonald: To reply to some of Dr. Pines's questions:

1. There is a fairly reasonable body of evidence that grain boundaries alone are not responsible for the anomaly. In particular Pearson looked at the thermoelectric power of pure copper down to low temperatures, strained the specimen, and looked at it again: there was still no sign of the marked minimum of thermoelectric power characteristic of the anomaly.

2. The residual resistance is found to be fairly closely a linear function of the concentration of impurities. This would seem to rule out appreciable clustering.

3. In copper-tin alloys the size of the minimum first increases with concentration, and then saturates.

Pines: I agree that grain boundaries will not give more than a dirt effect, and are not the main cause of the anomaly.

Korringa: Professor Gorter has suggested (see the end of Schmitt's paper) the existence of ferromagnetic domains antiferromagnetically combined. If these domains are fairly large, then we expect polarization of the conduction electrons and thus a splitting or wide broadening of the nuclear resonance spectrum; in fact this is not observed, nor is there an additional Knight shift.

Schmitt: The lack of additional Knight shift in these alloys is based on one experiment only, on an unannealed copper containing 0.29 atomic % manganese.

Gorter: We have also done it at Leyden. The Knight shift is slightly decreased.

Schmitt: I did not realize that this experiment had been repeated.

Gorter: Not repeated—carried out independently.

Sondheimer: May I end with a frivolous question, which I think may yet have some point. We can easily explain how a resistance minimum could be obtained in the presence of a magnetic field, if the magnetoresistance is large enough. The question is: why does the minimum stay when we take away the magnetic field?

NUCLEAR MAGNETIC RESONANCE AND ELECTRONIC STRUCTURE OF CONDUCTORS¹

BY N. BLOEMBERGEN²

ABSTRACT

The information about electron wave functions and band structures obtainable from nuclear magnetic resonance experiments in conductors is reviewed. The isotropic and anisotropic metallic shift, the relaxation time, isotropic and anisotropic spin exchange coupling, and quadrupole interactions are discussed. The variation of these effects as a function of pressure, temperature, and alloy composition is described. Some recent results for semiconductors and superconductors are included in the discussion.

I. THE METALLIC LINE SHIFT

When a metal is placed in a magnetic field H_0 , the electron spins are partially polarized, and give rise to the well-known Pauli spin paramagnetic susceptibility χ_P per unit volume. The polarization of the electron spins in turn produces a field at the position of the nuclei. This field is larger than the space-averaged magnetization because of the enhancement of the electronic S -type wave function near the nucleus. This additional field ΔH should be added to H_0 to determine the magnetic resonance condition of the nuclear spins. Knight (1) has recently given an extensive review of the experimental and theoretical aspects of this shift. Its main features follow directly from its origin outlined above:

- (1) The nuclear resonance in metals is always shifted toward higher frequencies for a fixed external field H_0 .
- (2) The shift is proportional to H_0 .
- (3) The shift is largely independent of temperature.
- (4) It becomes progressively larger for elements with higher atomic number.
- (5) It is relatively smaller, if the wave function of the conduction electrons has a predominant lack of S -character.

These characteristics are contained in the theoretical expression

$$(1) \quad \frac{\Delta\nu}{\nu_0} = \frac{\Delta H}{H_0} = \frac{8\pi}{3} \chi_P \Omega \langle |\psi(0)|^2 \rangle_F \equiv \frac{8\pi}{3} \chi_P \Omega P_F,$$

where the average is taken over the Fermi surface. The wave function ψ is normalized over the atomic volume Ω . Eq. (1) is also valid for semiconductors, provided a suitable average of $|\psi(0)|^2$ is taken over the Maxwell-Boltzmann distribution. The susceptibility for the electron gas in semiconductors is very small. No detectable shift has been reported.

In metals $\Delta\nu/\nu_0$ and $\chi_P \Omega$ can be measured experimentally, and $\langle |\psi(0)|^2 \rangle_F$ derived from Eq. (1). The frequency shift can be determined with great accuracy, but a difficulty lies in the establishment of a proper reference. In

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comparing the resonance frequency in the metal and in an insulating compound, a correction has to be made for the different orbital contributions (chemical shifts) in the two cases. Fortunately the error introduced in this manner is usually small, as the Knight shift is much larger than these chemical shifts. It can be rigorously eliminated, if the conduction electron spins can be saturated simultaneously by applying a resonant radiofrequency magnetic field to them. The Knight shift then reduces to zero, while the diamagnetic contributions remain. This technique is possible in the alkali metals and beryllium. The simultaneous occurrence of the Overhauser polarization is of no concern here (2). In other metals no electron spin resonance has been found because of strong electron spin-orbit coupling.

The experimental determination of χ_P offers more serious difficulties. A poorly known diamagnetic contribution has to be subtracted from experimentally observed d-c. susceptibilities. Schumacher and Slichter (3) have shown an elegant way in which this difficulty can be overcome in metals with observable electron spin resonance. The total integrated nuclear spin and electron spin resonance absorption is measured at the same frequency in the same sample by varying the external field. The electron spin susceptibility is thus calibrated in terms of the nuclear spin susceptibility, which follows the simple Curie law.

Accurate theoretical calculations for χ_P based on the collective electron model can be found in Pines' review article (4). This model holds very well for the alkali metals, where a direct comparison with experimental values is possible. The correlation effects modify the value of the spin susceptibility substantially from the free electron value and give a different volume dependence.

Theoretical calculations of the electron density at the nucleus are only available for the alkali metals. They are based on the Wigner-Seitz cell method (5). Kohn (6) used the refinement of a variational technique. Brooks and Ham used the quantum defect method. Both methods give accurate values of the cohesive energy and effective mass as a function of atomic volume, but also the value of the wave function at the nucleus.

Since both the theoretical and experimental situation favor the investigation of the alkali metals, some more detailed results will be presented in the next section. In general we shall place more emphasis in this paper on those topics which supplement rather than duplicate Knight's comprehensive review.

II. THE PRESSURE AND TEMPERATURE DEPENDENCE OF THE SHIFT IN ALKALI METALS

Theoretical and experimental values for $\chi_P\Omega$, and P_F for the alkali metals at room temperatures and atmospheric pressure are shown in Table I. The values of m^*/m have been calculated by Brooks (7). It is seen that Kohn's calculation for P_F gives the best agreement with experiment. Brooks, however, obtains a more accurate volume dependence of P_F . This quantity is experimentally determined by measuring the Knight shift as a function of hydrostatic pressure. Figs. 1 and 2 show the results for lithium and sodium recently obtained by

TABLE I
THEORETICAL AND EXPERIMENTAL VALUES OF χ_P AND P_F

	m^*/m	$\Delta\nu/\nu$	$(\chi_P)_{\text{exp}}$	$(\chi_P)_{\text{th}}$	$(P_F)_{\text{exp}}$	$(P_F)_{\text{Kohn}}$	$(P_F)_{\text{Brooks}}$
Li	1.35	0.0249%	2.08 ± 0.1	1.71	0.125	0.11 ± 0.1	0.107
Na	0.98	0.113%	0.95 ± 0.1	0.85	0.616	0.605 ± 0.03	0.66
Rb	0.89	0.653%		0.51	2.63		
Cs	0.83	1.49%		0.42	5.9		
Cu	1.0	0.232%		1.31	2.62		

χ_P is in c.g.s. volume units $\times 10^6$.

P_F is in Bohr units (a_0^{-3}).

The effective mass m^* has been calculated by Brooks (7).

$(\chi_P)_{\text{exp}}$ is determined by Schumacher and Slichter (3).

$(\chi_P)_{\text{th}}$ is determined by Pines (4) on the basis of the collective electron model.

$(P_F)_{\text{exp}}$ is calculated from $\Delta\nu$ and $(\chi_P)_{\text{th}}$.

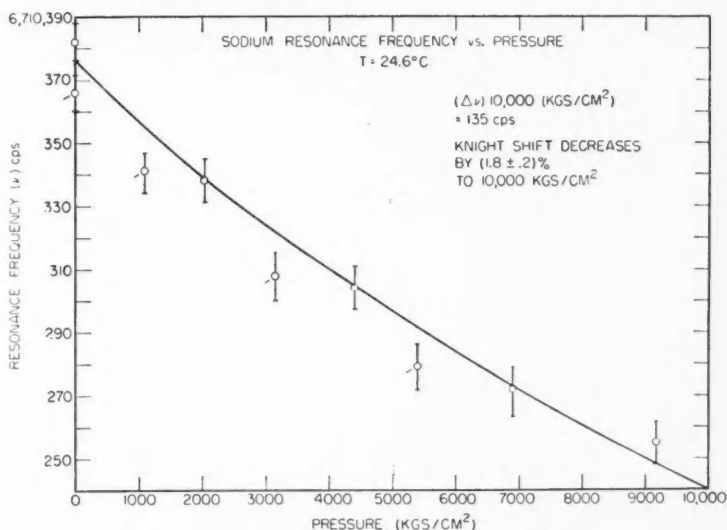


FIG. 1. The variation of the nuclear resonance frequency at 5940 oersteds with hydrostatic pressure in sodium at 24.6°C.

Benedek and Kushida (8). The change in the Knight shift at 10,000 atmospheres amounts to only 100 c.p.s. in 6 Mc./sec. With the aid of a very stable reference oscillator, the resonant frequency can be measured with a precision of about 10 c.p.s.

The narrowness of resonances is an important factor in obtaining this precision. The lines in the alkali metals are narrowed by self-diffusion. Lithium had to be heated to 80°C. to obtain sufficient narrowing. This is another experimental advantage of the alkali metals. Other metals may show narrowing by self-diffusion close to their melting points, but thus far no such experiments have been reported. Nuclear resonance may be used to determine the coefficient of self-diffusion as a function of temperature and pressure.

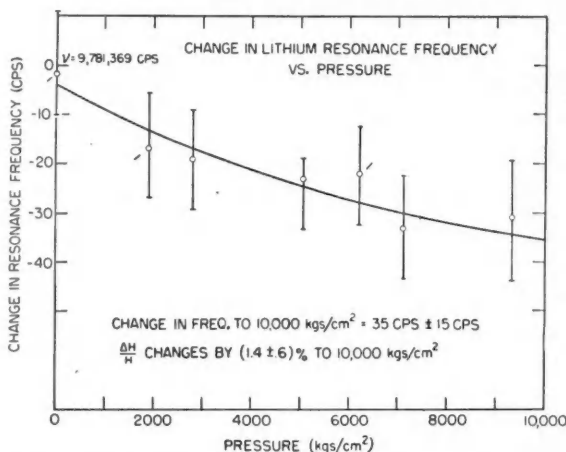


FIG. 2. The variation of the nuclear resonance frequency at 5919 oersteds with hydrostatic pressure in lithium at 80° C.

In Table II the experimental volume dependence, derived from Figs. 1 and 2 and Bridgman's values for the compressibility, is compared with the theoretical

TABLE II
VOLUME DEPENDENCE OF $\Delta\nu/\nu$, $(\chi_p)_{th}$, AND P_F

	$\frac{\partial \ln m^*}{\partial \ln V}$	$\frac{\partial \ln \Delta\nu}{\partial \ln V}$	$\frac{\partial \ln (\chi_p)_{th} \Omega}{\partial \ln V}$	$\frac{\partial \ln (P_F)_{exp}}{\partial \ln V}$	$\frac{\partial \ln (P_F)_{Kohn}}{\partial \ln V}$	$\frac{\partial \ln (P_F)_{Brooks}}{\partial \ln V}$
Li	-0.445	$0.18 \pm .08$	-0.03	+0.21		$+0.7 \pm 0.4$
Na	0	$0.15 \pm .02$	+0.60	-0.45	-0.26	-0.43

results. The agreement with Brooks' theory for sodium is excellent. The theoretical volume dependence for lithium is very uncertain because of poor convergence of a perturbation procedure near the Fermi level in lithium. The agreement for both metals would be less good if a free electron model rather than Pines' collective model were used.*

The temperature dependence of the shift in the alkali metals has been observed by Gutowski (9) and by Knight (10). They report a 2% increase in $\Delta\nu/\nu_0$ in going from 200° K. to 350° K. Originally this temperature variation was interpreted in terms of a volume variation of 3.1% through expansion over the mentioned temperature interval. The pressure data show that only a 0.45% increase in $\Delta\nu/\nu_0$ is due to this effect. The remaining variation of $1.5 \pm 0.1\%$ is caused by a specific effect of the lattice vibrations. The electron wave functions and consequently P_F follow adiabatically the changes in the

*In Eq. (9.14) of Pines' paper the last two terms should be proportional to r_s^{-1} and r_s respectively. The first term depends also on the volume through the effective mass. These corrections have been incorporated in Table II.

atomic polyhedron due to thermal strain. The shape variations will be relatively unimportant, as the wave function of the conduction electron is very flat near the boundary of the atomic polyhedron. Shear deformation will therefore be neglected, consistent with the Wigner-Seitz replacement of the polyhedron by a sphere of equal volume. Fuchs (11) introduced similar assumptions in the calculation of the elastic constants. Volume variation will produce a change in P_F which was discussed in the preceding paragraph. The average effect of the thermal vibrations is not zero because P_F is not a linear function of Ω ,

$$(2) \quad \langle P_F \rangle_{\text{vibr}} = P_F + \left(\frac{\partial^2 P_F}{\partial V^2} \right)_{\Omega} \langle \Delta V^2 \rangle_{\text{Av.}}$$

Using a Debye model for the compressional elastic waves one finds readily

$$(3) \quad \langle (\Delta V)^2 \rangle_{\text{Av}} = \frac{V^2}{dc^2} \int_0^{\nu_{\text{max}}} \frac{4\pi\nu^2}{c^3} h\nu \left(\frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1} \right) d\nu,$$

where d is the mass density and c the velocity of the longitudinal waves.

For very short waves, with wave length comparable to the interatomic distance, this derivation lacks rigor. The assumption was made that the whole lattice is deformed uniformly. For short waves neighboring cells will have different atomic volume and the problem of wave function matching would become very difficult. Eqs. (2) and (3) probably give a good semiquantitative description of the temperature effect. With the value $(\Omega^2/P_F)(\partial^2 P_F/\partial V^2)_{\Omega} = 0.95$ derived from Brooks' calculation of $P_F(V)$ for sodium, one finds a variation of the Knight shift of 2.1% between 200° K. and 350° K. This is in good agreement with the experimental contribution of the lattice vibrations to the shift. At high temperatures the effect, which according to Eq. (10) is proportional to the thermal energy, is a linear function of T . Below the Debye temperature it drops rapidly. Knight has observed a relative decrease of the shift at 4° K. which is much larger than predicted by Eqs. (2) and (3). The experimental accuracy is, however, not great as the line is broad at low temperatures.

Zero-point vibration adds 0.75% to P_F in sodium. The experimental value in Table I should be diminished by this correction before comparison with the theoretical values. The corresponding correction for lithium will have the opposite sign and will be relatively larger.

No correction of the thermal motion to the susceptibility χ_F has to be made, although this quantity is also a non-linear function of volume. The electron spins do not have the opportunity to come into equilibrium at the instantaneous volume in a thermal wave. The electron spin lattice relaxation time (12) in lithium and sodium at 300° K. is longer than 10^{-9} sec. This is much longer than the period of a characteristic lattice vibration (10^{-12} sec.).

III. VARIATION OF THE SHIFT IN ALLOYS

Although the experimental information is still rather meager (1), the following facts are striking:

(1) The resonance frequency of both the solvent and solute atoms is nearly independent of composition in a given phase.

(2) Discontinuous frequency jumps occur across a phase boundary. In Table III the experimental results of Teeters in the copper-aluminum system

TABLE III
KNIGHT SHIFTS IN THE Al-Cu SYSTEM

Per cent Cu	$[\Delta H/H_0]_{\text{Cu}}^{63}$	$[\Delta H/H_0]_{\text{Al}}^{27}$
100	0.228×10^{-2}	
95	0.231	0.112×10^{-2}
90	0.226	0.104
85	0.226	0.102
5	0.205	0.155
0		0.162

are reproduced. Friedel has given an elegant explanation, based on the theory of a Thomas-Fermi electron gas, ignoring correlation effects. Introduce the charge density of electrons with an energy less than E , measured relative to a free electron outside the metal,

$$\rho(E, \mathbf{r}) = \int^E \psi^*(\mathbf{r}) \psi(\mathbf{r}) n(E) dE$$

where $n(E)$ is the density of states. A basic theorem, due to von Laue, states that $\rho(E, \mathbf{r})$ is independent of the boundary conditions in a volume of constant potential. In an alloy the potential away from a solute atom is unchanged, owing to the extremely good shielding by the gas of conduction electrons. Consequently the charge density is constant even for high alloying concentrations c ,

$$\partial \rho(E, \mathbf{r}) / \partial c = 0,$$

$$\frac{\partial}{\partial E} \frac{\partial \rho(E, \mathbf{r})}{\partial c} = \frac{\partial}{\partial c} \{ \psi^* \psi n(E) \} = 0.$$

The equations hold for any value of E and \mathbf{r} .

In particular the variation of the Knight shift vanishes, because

$$\frac{\partial}{\partial c} \{ \psi^*(0) \psi(0) n(E_F) \} = 0.$$

The variation in the density of states is exactly compensated by the redistribution of the single electron wave functions normalized over the whole lattice in the neighborhood of the impurity. The interesting fact is that this law seems to hold so well even for very high concentrations. Apparently detailed matching of impurity wave functions to the matrix wave functions plays a minor role. Some idea about the behavior of the wave function in the alloy may be obtained by comparing the ratio of the Knight shifts of the two constituents to the ratio of the hyperfine interactions in the corresponding atomic S -states. In this connection it would also be very interesting, for example, to measure the Ag-resonance in Ag-Au through all compositions of the complete solid solution, and to investigate the effect of ordering, for example, in Cu-Au system on the shift. Interference of quadrupole effects in alloys makes systems with nuclear spins $I = 1/2$ most desirable for Knight shift investigations.

Little work has been done so far on liquid metals and alloys and this undoubtedly will prove another fruitful field of investigation.

IV. ANISOTROPIC METALLIC SHIFT

In general the relation between the internal field ΔH and the external field has tensor character. In non-cubic crystals there is the phenomenological possibility for an anisotropy of the shift. In crystals with axial symmetry it will vary as $\cos^2\theta$, where θ is the angle between H_0 and the symmetry axis. Such an anisotropy has been observed in tetragonal tin (14, 15) and hexagonal cadmium (16). Data are given in Table IV. Since the samples are always in

TABLE IV
ANISOTROPY OF KNIGHT SHIFT

	$[\Delta H/H_0]_{ }$	$[\Delta H/H_0]_{\perp}$
Cd ^{111,113}	$0.444 \pm 0.004\%$	$0.401 \pm 0.004\%$
Sn ^{117,119}	$0.79 \pm 0.005\%$	$0.75 \pm 0.005\%$

finely dispersed powdered form to allow the radiofrequency field to penetrate through the metal particles, the observed effect consists of a characteristic asymmetric broadening, proportional to the field H_0 . The effect is caused by the magnetic dipole interaction between the magnetized electron spins and the nuclear spin in orbitals with an unbalanced p -, d -, etc. character. Part of the anisotropy may also be due to an anisotropy in the electron g -factor,

$$\frac{\Delta\nu_{||} - \Delta\nu_{\perp}}{\nu_0} = \frac{3}{2}\chi_F\Omega q_F + \frac{g_{||} - g_{\perp}}{g_{AV}}\Delta\nu_{1s}.$$

Here q_F is a measure of the asymmetry in the electron charge density,

$$q_F = \langle \int \psi^* r^{-5} (3z^2 - r^2) \psi d\mathbf{r} \rangle_F,$$

where the axis of symmetry is taken in the z -direction.

Unfortunately the two quantities q_F and $g_{||} - g_{\perp}$ cannot be separated experimentally. No electron spin resonance has been observed in non-cubic metals, except beryllium. Here the anisotropy seems to be zero. There is no observable Knight shift in this metal (1). Anisotropy of the shift has been observed in solid mercury. No reliable evaluation of the data is available in this case.

V. SPIN-LATTICE RELAXATION

The hyperfine interaction between electron and nuclear spin also often provides the dominant relaxation mechanism in conductors. On the assumption that the dominant term is the isotropic or "s-type" hyperfine interaction, Korringa derived a simple relation between the relaxation time T_1 and the shift $\Delta\nu$. Pines has refined this relation by pointing out that the relaxation effect is adequately described by the density-of-state function of an electron gas with correlation, but that the spin susceptibility and consequently the shift are modified more intricately by the correlation. Pines (4) adds therefore two correction factors to the Korringa relation

$$(4) \quad T_1 \left(\frac{\Delta \nu}{\nu_0} \right)^2 = \frac{\hbar}{4\pi k T} \left(\frac{\gamma_e}{\gamma_N} \right)^2 \left\{ \frac{\rho_0(E_F)}{\rho(E_F)} \right\}^2 \left(\frac{\chi_F}{\chi_0} \right)^2;$$

$\rho_0(E)$ and χ_0 are the density of states and spin susceptibility for the free electron gas,

$\rho(E)$ and χ_F are their counterparts for the actual gas of interacting electrons.

Table V compares the experimental results of T_1 with values calculated from Eq. (4) under the assumption $\rho/\rho_0 = 1$.

TABLE V

NUCLEAR SPIN-LATTICE RELAXATION TIMES AT ROOM TEMPERATURE (IN MILLISECONDS); THE EXPERIMENTAL DATA ARE TAKEN FROM NORBERG (17) AND REDFIELD (18), AND THEORETICAL DATA ARE CALCULATED FROM EQ. (4)

	m^*/m	$(T_1)_{\text{exp}}$	$(T_1)_{\text{th}}$
Li ⁷	1.45	150	232
Na ²³	0.98	15.9	18.1
Rb ⁸⁵	0.89	2.75	2.94
Cu ⁶³	1.0	3.55	4.0
Al ²⁷	1.0	5.5	6.5

It is reassuring that the experimental values are consistently somewhat smaller. The "non- s " magnetic dipole interaction and the electric quadrupole interaction will also make a contribution to the relaxation mechanism even in cubic crystals. Since the hyperfine interaction for an s -state is so much larger, the Korringa relation is approximately fulfilled even if the electron wave function at the Fermi level has less than 50% s -character. More accurate determination of T_1 in other metals may give an estimate of the percentage of "non- s " character in the wave function at the Fermi level. The anisotropic shift gives an idea about the unbalance of "non- s " character in non-cubic crystals. Redfield (18) has checked the validity of (4) over a large temperature interval, from 2° K. to 300° K., for Cu and Al. Norberg (17) finds some discrepancy in the dependence on H_0 . The relaxation time T_1 , which should be independent of H_0 , actually increases by 10–15% if the magnetic field is increased by a factor three.

Although the density of conduction electrons in semiconductors is much smaller than in metals, they still can provide the dominant relaxation mechanism if quadrupole interactions are absent ($I = \frac{1}{2}$). Bloembergen (19) has extended Korringa's theory to an electron gas of low density, obeying Maxwell-Boltzmann statistics. The effect of an anisotropic mass with principal values m_1 , m_2 , and m_3 and interband scattering between l bands is taken into account by Anderson. The relaxation time is given by (Ref. 20)

$$(5) \quad \frac{1}{2T_1} = \frac{256\pi\beta^2\gamma_N^2 I^2 N |\psi(0)|^2 \Omega}{9\hbar^2} \left(\frac{m_1 m_2 m_3 k T}{2\pi} \right)^{1/2};$$

N is the density of mobile carriers, β is the Bohr magneton, $|\psi(0)|^2$ is a suitable average over the Boltzmann distribution, for which the value at the band edge may be taken.

Recent experimental results on T_1 in n - and p -type silicon, obtained by Shulman (20), are plotted in Fig. 3. The proportionality to the carrier density is well established. At low concentration ($N < 10^{15}$) another mechanism apparently takes over. This may be spin diffusion to paramagnetic impurity

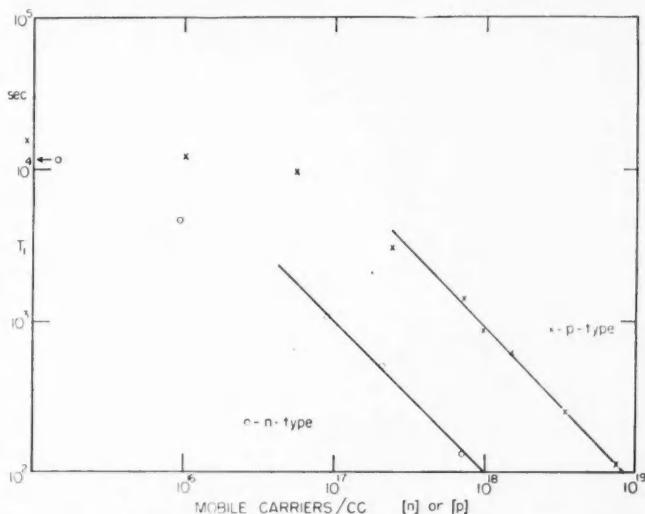


FIG. 3. The relaxation time of the Si^{29} resonance in n - and p -type silicon at room temperature (20).

levels. This process was expected to be more effective (19). The relaxation time in p -type material is even longer than in n -type at the same carrier concentration. This is due to the predominant p -character of the hole wave functions. In fact, Eq. (5) would have to be modified somewhat to take account of relaxation by p -type hyperfine interaction. Experiments on the dependence of T_1 on temperature and impurity concentration are in progress. It will be of special interest to find out how T_1 behaves when impurity band conduction occurs.

VI. ELECTRON COUPLED NUCLEAR SPIN INTERACTIONS

The interaction between a nuclear spin and the electron spin perturbs the electron wave function slightly. The perturbed electronic state may interact in turn with another nuclear spin. In second-order approximation an interaction between two nuclear spins results, which is proportional to the square of the hyperfine interaction. For solids the process is schematized in Fig. 4. An electron with momentum \mathbf{k} is virtually scattered to an unoccupied intermediate state \mathbf{k}' by a nuclear spin and scattered back into the initial state by another nuclear spin. The process can occur in conductors and insulators. There is no conservation of momentum in each scattering process, because the perturbation by the random nuclear spins has no periodic character. The isotropic hyperfine

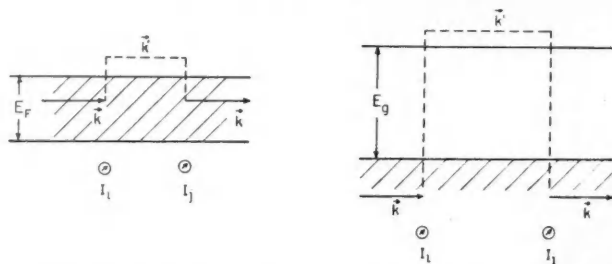


FIG. 4. Schematized electron coupled nuclear spin interaction in a metal and an insulator. E_F is the Fermi energy, E_g is the forbidden energy gap. The electrons are virtually scattered by the interaction of their spin with the nuclear spins I_i and I_j .

interaction will usually be dominant. If Bloch-type one-electron wave functions $\psi_{\mathbf{k}} = u_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}$ are used, it gives rise to a nuclear spin exchange interaction

$$(6) \quad \mathfrak{H}_{ij}^{\text{ex}} = A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j,$$

$$(7) \quad A_{ij} = [2 \operatorname{Re} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \Delta_i(\mathbf{k}, \mathbf{k}') \Delta_j(\mathbf{k}, \mathbf{k}') \exp[i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{R}_i - \mathbf{R}_j)] \times \{E(\mathbf{k}) - E(\mathbf{k}')\}^{-1}].$$

The isotropic hyperfine interaction is contained in the function

$$(8) \quad \Delta_i(\mathbf{k}, \mathbf{k}') = \Delta_i^*(\mathbf{k}', \mathbf{k}) = \frac{16\pi}{3} \gamma_N \hbar \beta u_{\mathbf{k}}(R_i) u_{\mathbf{k}'}^*(R_i).$$

The summations extend over all occupied states \mathbf{k} with energy $E(\mathbf{k})$ and all unoccupied intermediate states \mathbf{k}' with energy $E(\mathbf{k}')$. The result of the integrations over the conduction band in metals has been given by Ruderman and Kittel (21). Integrations over the valence and conduction bands in insulators have been carried out by Bloembergen (22). At large distances, the interaction decreases as R_{ij}^{-3} in metals, and exponentially in insulators. Anderson (23) has pointed out that for near neighbors large regions of the band structure contribute to A_{ij} , both in metals and in insulators, provided the energy gap is not too large, $(2mE_g)^{1/2} \hbar^{-1} R_{ij} \ll 1$. A complicated average of the hyperfine interaction (Eq. (8)) over the band structure, weighted by the inverse energy difference, results. This average cannot be directly compared with the hyperfine interaction at the Fermi level, derived from Knight shift and relaxation time. Using an oversimplified band model of a free electron gas, Bloembergen (22) derives that the two quantities differ by a factor 1.7 for thallium. His derivation of the sign of the exchange constant is unwarranted. Accurate numerical integrations over the band structure are necessary.

The hyperfine interaction of that part of the electron wave function which does not have s -character gives rise to a pseudo-dipolar interaction between the nuclear spins, characterized by a phenomenological constant B_{ij} . The theoretical expression (22) for B_{ij} consists again of appropriate summations over the band structure. This interaction interferes with the ordinary dipolar interaction,

$$(9) \quad \mathfrak{H}_{ij}^{\text{tensor}} = (\gamma_i \gamma_j \hbar^2 R_{ij}^{-3} + B_{ij}) \{ \mathbf{I}_i \cdot \mathbf{I}_j - 3 R_{ij}^{-2} (\mathbf{I}_i \cdot \mathbf{R}_{ij}) (\mathbf{I}_j \cdot \mathbf{R}_{ij}) \}.$$

Experimentally the presence of the electron-coupled interactions is detected by their influence on the width and shape of the resonance line. The effect of the exchange interactions A_{ij} is especially noteworthy. When nuclear spins i and j have the same resonant frequency, the interaction will cause an exchange narrowing; when the resonant frequencies are different, exchange broadening occurs. The exchange interaction in solids was first discovered and identified (22) by varying the isotopic concentration of Tl^{203} and Tl^{205} in thallium and thallium oxide. The exchange narrowing in pure Tl^{205} was not pronounced, because of a large pseudo-dipolar interaction B_{ij} . This indicates a preponderant "non- s " character of the conduction band in thallium. For light nuclei the ordinary dipolar interaction will prevail; for heavy nuclei the exchange interactions will be larger because of the increasing hyperfine interaction. For silver the ratio of exchange and dipolar interaction is of the order unity.

An average value of the A_{ij} and B_{ij} is determined from the observed line width. Contribution from nearest neighbors will however be dominant. Further separation of the constants involved may be achieved by observing the line width as a function of isotopic constitution. By this technique Shulman's data (24) for indium and gallium antimonide could be amplified considerably. Shulman showed that his results are consistent with reasonable models for the band structure. In particular a very simple empty-lattice model or free electron gas with 25% s -character of the wave function in this diamond-type lattice gives the correct order of magnitude. This clearly shows that not just the band edges contribute to the effect. Some published experimental data are listed in Table VI. Results for insulators (thallium and alkali halides and thallium oxide) are not included.

TABLE VI
DIPOLAR, EXCHANGE, AND PSEUDO-DIPOLAR INTERACTION
BETWEEN NEAREST NEIGHBORS IN KC./SEC.

	$\gamma\gamma_2\hbar R_{12}^{-3}/4\pi^2$	$A_{12}\hbar^{-1}$	$B_{12}\hbar^{-1}$
Thallium	1.0	15.5	4.5 or (-6.5)
Silver	0.017	0.024	
Indium antimonide	0.23	1.8	
Gallium antimonide	0.14	0.82	

It is tempting to apply the calculation outlined in this section to the interaction between ion cores in ferromagnetic metals. Whereas the nuclear spins provide a really small perturbation to the electronic states, the overlap between core and conduction electron wave functions is not a small perturbation. The related controversies on the theory of ferromagnetism (25) will not be discussed here. It is interesting to point out, however, the relative simplicity of the theory of nuclear ferromagnetism.

Difficulties already arise when the interaction of a nuclear spin with the electron spin of a dissolved magnetic impurity atom is considered. Experimental data are available (26) for dilute solutions of manganese in copper. At low temperatures the line becomes broad. This could be expected on the basis of an exchange interaction between electron and nuclear spin. The ordinary dipolar interaction is not sufficient to explain the broadening and

shortening of the nuclear relaxation time. At high temperatures these interactions are averaged out owing to rapid fluctuations of the electron spin orientation. One would expect, however, that there would also be a considerable displacement of the nuclear resonance, because the impurity atoms, and therefore the conduction electrons, acquire a considerable net magnetization. An enlarged Knight shift was not observed.

The observation of the nuclear resonance in the transition metals V and Nb provides evidence that the expectation value of the spin magnetization on each atom is zero (27).

VII. QUADRUPOLE INTERACTION

In non-cubic crystals with nuclear spin $I > \frac{1}{2}$ quadrupole interactions exist. The symmetry around an individual nucleus rather than the over-all symmetry of the lattice counts. Pronounced quadrupole effects on the Cu^{63} and Al^{27} resonances have been found (14, 15) in solid solutions in an aluminum or copper matrix. On the other hand, the $\text{Ga}^{69,71}$ resonance of gallium atoms, dissolved at low concentration in a copper lattice, shows no quadrupole interaction (1).

In solid solutions the magnitude and the orientation of the electric field gradient tensor will vary throughout the lattice. In powdered samples of metals and intermetallic compounds only the orientation will vary. In the presence of an external magnetic field, a distribution of resonant frequencies will result, which often makes the line partially or completely unobservable. In beryllium a quadrupole broadened resonance with characteristic shape has been detected, from which Knight (28) deduced the rather small quadrupole interaction of 12 kc./sec.

In zero magnetic field a so-called pure quadrupole resonance can be observed in metals and intermetallic compounds. Knight (29) has found such resonances at 10.908 Mc./sec. for Ga^{69} and at 6.866 Mc./sec. for Ga^{71} in solid gallium. The frequencies increase by about 3% when gallium is cooled from 0° C. to -196° C. The contribution of all charges in the lattice, including the conduction electrons, to the electric field gradient can thus be measured, if the quadrupole moment of the nuclei is known.

The electric field gradient around a solute atom in a solid solution decreases rapidly with distance as could be expected. The effect of dislocations and vacancies has also been detected (15). A quantitative interpretation of the experimental results will be very difficult. In the first place, these results are averages over many lattice sites and orientations. Furthermore, the contributions of ion core distortion, ion core polarization, and of the charge distribution of the conduction electrons cannot be separated. Much more experimental work is needed to obtain at least a qualitative insight into the charge distribution around solute atoms.

An interesting case is the solution of germanium of III-V compounds like Ga Sb. Conductivity measurements indicate that a pair of Ge-atoms replace a Ga Sb molecule. The quadrupole interaction of the Ga Sb nuclei will give further information about the structure of this alloy.

Ordering effects may also be studied. The fact that in pure III-V compounds the intensity of nuclear spin absorption is close to the theoretical value indicates absence of quadrupole broadening. A nearly perfect order exists in these compounds. For further information on quadrupole effects the reader is referred to an earlier review (15) and to a forthcoming one (30).

The role of the quadrupole interaction in relaxation processes has already been mentioned. The quadrupole interaction with the conduction electrons is usually smaller than the electron spin interactions, as it causes only a deviation from the interval rule of the magnetic hyperfine interaction.

In semiconductors and insulators the fluctuating electric field gradients produced by the thermal deformations of lattice vibrations frequently determine the relaxation time. This is, for example, the case in gallium and indium antimonide (24), which therefore have a much shorter relaxation time than Si^{29} ($I = \frac{1}{2}$) in silicon.

VIII. SUPERCONDUCTORS

Recently nuclear magnetic resonance has been observed (31, 32) in superconducting mercury particles. Extremely fine colloidal particles, smaller than the superconducting depth λ , are required to obtain a reasonably uniform penetration of the d-c. field into the superconducting metal. Reif used a sample of Hg droplets with a diameter smaller than 10^{-5} cm. The most probable diameter was 2×10^{-6} cm. In a field of 6500 or 3300 oersteds only the nuclear resonance of the normal metal is observed. The line width is determined by the anisotropic Knight shift and spin exchange interactions between Hg^{199} and Hg^{201} . The isotropic part of the Knight shift is $2.4 \pm 0.1\%$. In fields of 1500 oersteds, or lower, a second absorption line of Hg^{199} appears on cooling the sample from 4.2° K. down to 1.45° K. The second resonance at lower frequency is due to nuclei in mercury droplets which have become superconducting. The width and shape of this resonance is determined by the distribution of the d-c. field inside each particle and the distribution of radii of all particles.

Knight (32) has observed the resonance line of the superconducting state at 5000 oersteds below 2° K. He finds $\Delta\nu/\nu_0 \leq 0.5\%$ in the superconducting state at high fields, whereas Reif finds $\Delta\nu/\nu_0 = 1.5\%$ at lower fields. The shift seems to increase rapidly towards the value of normal metal just below the transition temperature. There is as yet no satisfactory explanation for these experimental results, which should be considered with caution since the analysis of the observed resonance structure is difficult. Results on very thin metallic films may afford an easier interpretation. The fraction of normal conduction electrons is of course a function of both temperature and magnetic field in these small particles (33).

The spin-lattice relaxation time in the superconducting state is longer than in the normal state. It has not yet been ascertained whether the Korringa relation remains valid. It would be violated if the superconducting electrons contribute to the shift, but not to the relaxation mechanism. Careful measurements of the shift and the relaxation time as a function of temperature below

the transition temperature will give valuable information about the electron spins in the superconducting state.

Another interesting possibility of measuring the relaxation time in the superconducting state without observing the resonance in that state was proposed by Redfield (34). Observe the resonance in fairly large particles of the normal metal at a very low temperature such that the relaxation time in the normal state is at least several seconds. The magnetic field is adjusted close to the superconducting phase boundary. The magnetic field is then decreased slightly so that the metal becomes superconducting. After a certain time interval which can be varied, the metal is brought to the original state and the intensity of the resonance signal is measured immediately. The magnetization of the nuclear spins will have decreased exponentially with the relaxation time characteristic of the superconductor in this experiment. Some difficulties arise if the field inside the superconducting particles would drop to a value smaller than the internal field, $1/\gamma T_2$, produced by neighboring nuclear spins in a time shorter than T_2 . Under these circumstances the demagnetization of the nuclear spin system would not be adiabatic and the experiment would not give T_1 in the superconducting state.

The zero magnetic field pure quadrupole resonance could be observed in superconducting gallium. The particle size need not be smaller than the superconducting depth. Presumably the relaxation time would be determined by the interaction with the conduction electron spins. Nuclear spin diffusion through the superconducting depth is likely to be less important. A number of interesting possibilities apparently exist to probe into the electron spin properties of superconductors.

The author is indebted to G. B. Benedek, W. D. Knight, T. Kushida, A. G. Redfield, F. Reif, and R. G. Shulman for communication of results before publication.

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DISCUSSION OF BLOEMBERGEN'S PAPER

Seeger: Barrett has discovered that under cold work there is a transition in sodium to close-packed hexagonal structure at about 30° K. The hexagonal form might give interesting anisotropic effects.

Bloembergen: Knight has observed the resonance in sodium at low temperatures, and found an anomaly which he explains as due to the phase transition. But this experiment is not altogether simple, since there is resonance broadening due to the classical dipole interaction. All the things that I've shown are narrow because of motional narrowing.

Gorter: What experimental evidence is there concerning the hypothesis that the density of states $\rho(E)$ changes at very low temperatures, as discussed by Fröhlich and Bhatia after the papers of Gorter, Schmitt, and Korringa?

Bloembergen: Between 1° and 4° K. there is no indication that this occurs at all. The nuclear spin relaxation time continues to be proportional to $1/T$.

Gorter: How accurate is this experimentally?

Bloembergen: To within 10%.

Gorter: This may not be accurate enough.

Fröhlich (in reply to **Bloembergen**): Although one has a second-order process, it is associated with a first-order change in wavelength. One does get a change in the density of states.

Bardeen: Even though a second-order perturbation gives a change in $\rho(E)$, there are suggestions that higher order terms may cancel it out.

Fröhlich: Nabarro and I found a very simple method of treating the indirect coupling of nuclear spins by conduction electrons. Incidentally, a modification of this method can be developed to treat insulators.

Pines: Equation (4) gives us an experimental method of determining the density of states of the alkali metals and hence the electronic specific heat, quite independently of the calorimetric methods which give only the sum of the electronic and lattice terms. There appears moreover in sodium to be an inconsistency between the two methods. I am inclined to attribute this to a difficulty with the calorimetric method, since I believe that at present the resonance approach is the more accurate.

Seeger: Perhaps this again can be put down to the phase transition.

Chambers: Does the Knight shift in mercury tend to zero at 0° K., as one might expect in a superconductor?

Bloembergen: No. The values I gave were the asymptotic values.

Bardeen: A superconductor might well have a finite spin paramagnetism. In the usual treatments there is no need to assume equal numbers of electrons of each spin.

Fröhlich: If this is so one would have a different relaxation mechanism and a different temperature dependence.

Further contributions were made by **Gorter**, who mentioned briefly experiments on fine colloids; and by **Fawcett**, who discussed with **Bloembergen** the importance of pseudo-dipole interactions in broadening electron spin resonance lines.

ELECTRICAL AND THERMAL CONDUCTIVITY OF METALS¹

By K. MENDELSSOHN²

Whereas before the War our knowledge on the conduction processes in metals at low temperatures rested on electrical measurements in isolated temperature regions and on a few observations of the thermal resistance of superconductors, a wealth of experimental material has been amassed in the last 10 years. The results are not only available as original publications but have also been gathered into a number of excellent summaries (1). It is impossible to give a comprehensive survey of the whole field in the space of one hour and such a survey would, moreover, consist largely of a repetition of well-known work. The present report, therefore, deals mainly with recent unpublished work carried out at Oxford and will consider the published results of other workers only in so far as they are needed for an understanding of our own investigations. It is hoped that the lack of balance produced in this way will be restored by the contribution of others to the discussion.

The temperature dependence of the electrical resistivity of systematically investigated groups of metals shows a remarkable agreement with theory in the case of sodium and fairly well understood deviations from the simple pattern in the case of other metals. It is encouraging that the Bloch-Grüneisen model, which is merely a one-electron theory for quasi-free electrons, should be obeyed reasonably well in the case of that metal which for theoretical reasons can be regarded as the nearest approach to this pattern. Qualitatively successful attempts have been made to account for the deviations from the simple pattern by the introduction of a screening parameter. Conditions here are clearly too complex to allow us to expect quantitative solutions. There also remains the low temperature minimum in the resistance of some specimens of certain metals, notably gold and magnesium, which is probably due to some kind of lattice imperfection; possibly a specific impurity. In spite of a good deal of experimental and theoretical work, no solution has been found which fits all the observed cases.

More experimental data are also required on the electrical resistance of the transition metals. In 1933 de Haas and de Boer (2) measured platinum and found that at the lowest temperature the resistivity showed a component varying with T^2 . A few years ago this work was supplemented by Mrs. Olsen-Bär (3), who investigated the temperature dependence of the resistivity of the following transition metal specimens:

Metal	θ_D	R/R_{90}	n
Pt	225	3.5×10^{-3}	3.1
Pd	275	2.5×10^{-2}	2.7
Rh	370	2.0×10^{-2}	1.6
Ni	375	1.36×10^{-1}	2.4
Co	385	2.01×10^{-1}	2.2
Fe	420	2.22×10^{-1}	2.5

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

²Clarendon Laboratory, Oxford, England.

In this table θ_D denotes the Debye characteristic temperature, R/R_{90} the ratio of the residual resistance to that at 90° K., and n the observed average power law, T^n , of the resistivity. The latter can be seen to be in rough qualitative agreement with the ideal of a T^2 term at the lowest temperatures (Fig. 1), but for most cases the obtained data hardly justify any more detailed analysis.

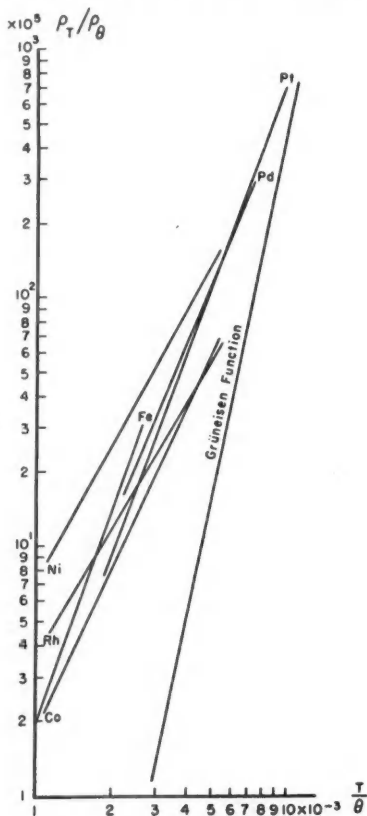


FIG. 1. Ideal resistance of the transition metals.

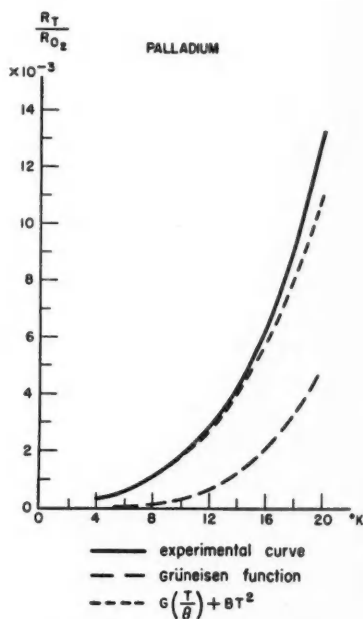


FIG. 2. Comparison of the resistance of Pd with a T^2 law.

De Haas and de Boer represented their results for the ideal resistance, ρ , of platinum by

$$(1) \quad \rho = aG(\theta_D/T) + BT^2,$$

where $G(\theta_D/T)$ is the Grüneisen function and a and B are constants. As shown in Fig. 2, a similar analysis was made by Mrs. Olsen-Bär of her results on palladium. The graph indicates that the attempt was only partly successful and that the agreement is not really good enough to be convincing of a simple addition of the two functions.

Here again the experimental data, while confirming the general trend in the behavior of the transition metals, are insufficient to form an adequate basis for theoretical interpretation. This work, while for technical reasons still unpublished, belongs to a period in which the method of simultaneous determination of electrical and thermal conductivity was not yet generally applied. It is clear that in future work on transition metals these two conductivities should be measured together, on very pure, zone-refined, single crystals.

The position is somewhat better in another section of her research which dealt with the resistivity of single crystals of gallium. This metal is highly anisotropic, and she together with Powell (4) could show that the strong anisotropy of the electrical resistance is maintained (or possibly slightly enhanced) down to the temperatures of liquid helium. The θ_D values derived for the three crystal directions from the electrical measurements are practically identical, being 131°, 132°, and 135° K. respectively at 6° K. It is somewhat surprising, and possibly accidental, that in this complex metal the power index n for the three specimens was ~ 4.5 below 12° K., which is close to the value postulated by Bloch for quasi-free electrons.

No simultaneous determination of the thermal resistance was carried out in this case, but since then Rosenberg (5) has measured this quantity for the three crystal directions between 2° and 40° K. on specimens which had been prepared by Dr. R. W. Powell from the same batch of metal. The thermal conductivity exhibited the same strong anisotropy above as well as below the maximum, which for these crystals is at about 8° K. The thermal resistance W followed the well-known equation

$$(2) \quad W = \alpha T^2 + \beta/T,$$

where α and β are the scattering parameters due to lattice vibrations and impurities. At 20° K., where the ratio of the electrical resistances is 1:2.7:8.9, α was found to have the values 1:4:10.5. The corresponding agreement of the β values, while broadly existing, was less close and this may be due to the fact that β is very sensitive to slight damage of the crystal.

Such damage can easily occur when mounting and attaching leads to the specimen, and its profound effect on the measured data makes this purely technical problem one of great importance in conductivity studies. Except for mechanically very strong specimens, one can never be sure that data obtained on the same specimen are comparable if it has been handled in the meantime. This is particularly the case when the thermal conduction is due to phonons, as will be shown later. Simultaneous measurement of electrical and thermal conductivities will therefore provide the only really reliable data, and it is also essential that the specimen should remain undisturbed *in situ* until all necessary information on it has been obtained.

Following up the relationship between electric and thermal conduction, provided by the Wiedemann-Franz law, it is only natural that the first aspect of the metal electrons to be studied should have been their contribution to the conduction process. The fair agreement found with equation 2, as is shown in particular by Rosenberg's (6) work on a large number of metals, indicates

that, certainly at low temperatures, the assessment of the factors leading to scattering of electrons has been on the whole correct. However, there is another aspect of the influence of electrons on the transport properties, and that is their own action as scattering centers. This second aspect has recently led to a quite astonishing amount of information and it has determined the course of most of our work in the last two years. It should be mentioned at the outset that we know as yet next to nothing about electron-electron scattering, about which further work on the transition metals may possibly give some information. Our experiments are thus largely concerned with the scattering of phonons by electrons and lattice faults.

The most obvious method of studying this problem is to interfere in one way or another with the conduction mechanism of the electrons and then to analyze the observed effect of this interference. The most straightforward way of doing this is by reducing electron conduction through the application of a magnetic field. These experiments have the advantage that the effects can be studied on one and the same specimen, whose structure remains undisturbed, and that the number of electrons remains constant. The more complex question of the detailed relation between conduction and crystal direction will not be considered here. It is clear that it may be possible to quench eventually with a high enough field the electron conduction completely, leaving only phonon conductivity. Experiments in Oxford (7), particularly on cadmium, yielded an increase in W by a factor 1000 in fields of 18 kilogauss but did not lead to any saturation, which means that the phonon conductivity, K_p , in a pure single crystal of Cd must be at least 10^4 times smaller than the electron conductivity, K_e .

More recent work by Alers (8) indicated the existence of such a saturation effect in a Zn single crystal of $K_0 = 4.78$ watt units at 3.5° K. Extrapolation to infinite field strength yielded a limiting value of $K = 0.5$ watt units. Since the anisotropy of K persists to the highest fields (in two other specimens) the author concludes, however, that the limiting value in this case is not identical with K_p . In the case of the value of $K_0 < 10^{-4} K_0$ obtained on the cadmium specimen in Oxford it is essential to be reminded that in this type of experiment the electrons, while being withdrawn partly from the conduction process, remain as scattering centers for phonons.

Another way of interfering with the electron conduction is to introduce into the specimen impurities which scatter electrons very effectively. In this context one should mention in particular the detailed work of Kemp and others (9), which has led to most interesting conclusions. The drawback of this method is that different specimens have to be compared with each other, and one will be somewhat uncertain whether strain and crystal size were the same in all cases.

Another, less obvious but more direct, method of finding out about the scattering of phonons by electrons is to change the number of the latter. One way of doing this is to use a lattice which is capable of accommodating a varying concentration of electrons, such as germanium. Since the discussion of thermal conduction of semiconductors falls outside the scope of this paper,

it should merely be mentioned that, in co-operation with Dr. Geballe of the Bell Telephone laboratories, Carruthers and Rosenberg in Oxford have measured the heat conduction of *p*-type germanium, containing from 10^{14} to 10^{19} group III impurity atoms per cc., between 2° and 90° K. The most impure of these samples shows semimetallic characteristics, and the results on the purest sample, which is effectively an insulator, have quite recently been extended to 0.2° K.

However, the most convenient way of changing the electron concentration is provided by superconductivity. As a metal is cooled to superconductivity, the "normal" electrons gradually disappear from the thermal distribution and pass into a state in which they do not interact with the phonons. While we know very little about the nature of this state, the disappearance of the phonon scattering by electrons has turned it into a valuable tool for the study of conduction processes in metals.

The effect of electron withdrawal on the thermal conduction is perhaps best illustrated by recent experiments of Rowell in Oxford on tantalum shown in Fig. 3. The lower values are obtained on a pure polycrystalline specimen which

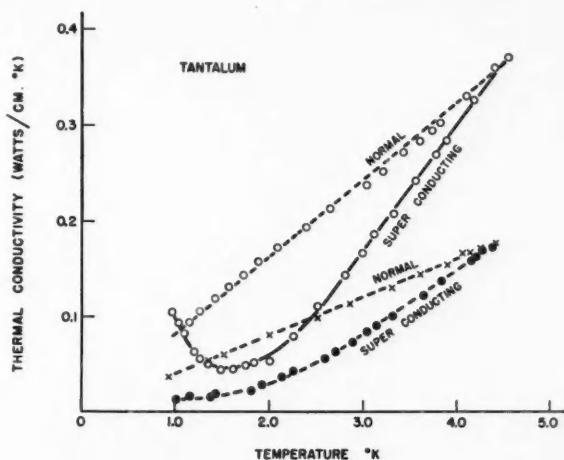


FIG. 3. Heat conductivity of tantalum.

is the same as used by Rosenberg in his general survey. At first sight the results seem to follow the conventional pattern as, for instance, found in tin. Closer examination shows, however, that K_s , the heat conduction in the superconductive state, does not extrapolate to zero at absolute zero. This trend was found to be much enhanced in a very pure, zone-refined, single crystal which was kindly put at our disposal by Services Electronics Research Laboratory, Baldock. This specimen shows the effect of greater purity by increased electrical and thermal conductivity in the normal state. What is remarkable in this case is the still stronger influence of purification on the superconductive

state. At the lowest temperatures there is a spectacular rise in K_s , which eventually becomes larger than K_n . This is the temperature region in which the concentration of normal electrons becomes very small and there is little doubt that the effect must be due to the reduced scattering of phonons by electrons. While we have found this behavior previously in alloys, where the scatter of electrons of the normal state had been greatly increased by the presence of foreign atoms, it had not so far been found in a pure metal where purification has decreased the heat resistance of the normal state.

The predominance of phonon conduction in pure superconductors was observed by us already some years ago in measurements on lead and other metals at temperatures below 1°K. , but in these cases K_s was always smaller than K_n . A plot of K_s/K_n against temperature, as shown in Fig. 4, clearly

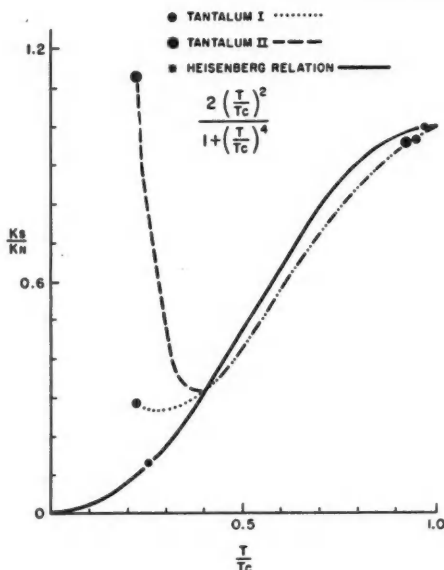


FIG. 4. K_s/K_n for tantalum.

reveals the rise in phonon conductivity also in the earlier specimen. It is, incidentally, interesting that the specimen Ta II shows a practically 100% Meissner effect and that the electronic entropy derived from the H_c/T -curve agrees well with the calorimetric data.

For a detailed study of heat flow phenomena in the superconductive state, lead is the most convenient metal since it has a low enough melting point to be prepared free of strain and a high enough transition temperature (7.2°K.) to allow the region of phonon conductivity to be studied at helium temperatures ($> 1^\circ \text{K.}$). Earlier experiments with Olsen (10) on the Pb-Bi system

revealed a number of interesting features, and a more comprehensive study has now been made by Montgomery (11) in Oxford.

Figure 5 giving the residual electric resistance ρ_0 of the specimens shows in the first place that it is proportional to the amount of each impurity and also that the charge of the ion as well as its size has a profound effect. Scattering is increased least by Sn which has the same valency as Pb. The effect is correspondingly larger for Tl and Pb as second component.

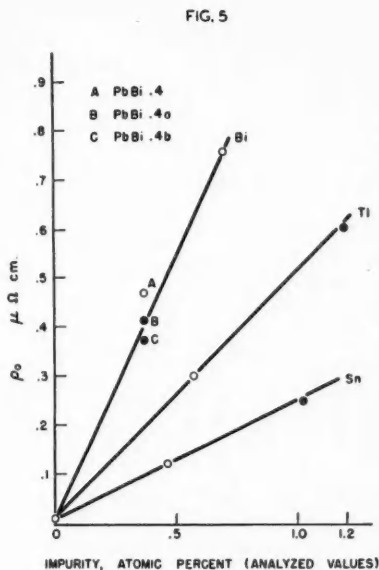


FIG. 5. Residual resistances of lead alloys.

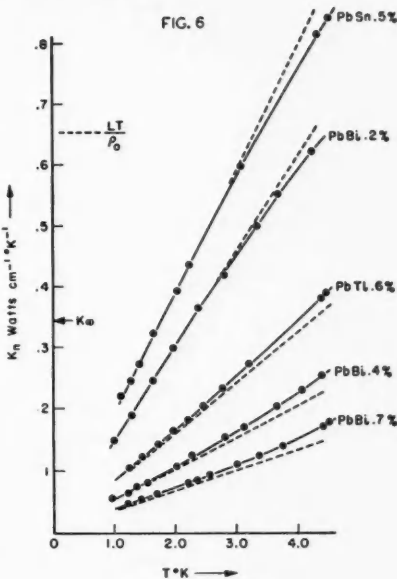


FIG. 6. K_n for some lead alloys.

Dealing first with the normal state we see from Fig. 6 that with growing impurity the position of K_n values with respect to $(LT)/\rho_0$ undergoes a change. While K_n falls short of $(LT)/\rho_0$ for the less impure specimens it rises above this value for Pb Tl 0.6%, and Pb Bi 0.4% and 0.7%, and it is reasonable to expect this to be lattice conduction. Theoretically we can expect

$$K_n = \frac{L_0 T}{\rho_0} + AT^2 - \frac{aL_0^2 T^4}{\rho_0^2}$$

with A (the parameter for the phonon conduction) having the value

$$\frac{4.93 K_\infty}{N_a^2 \theta_D^2}$$

In cases where the third term can be neglected, a quantitative analysis can be made by plotting K_n/T against T , which should yield straight lines of slope A and intercept L_0/ρ_0 . The third term can be neglected for the two Pb Bi

specimens, and there seems to exist a reasonable agreement with the T^2 law (Fig. 7). For the Pb Tl alloy, α has been taken as 3×10^{-3} watt units, the third term contributing about 30%. In the latter case the values for both the annealed and the work-hardened specimen have been included and the agreement between the two sets suggests that the scatter of phonons is entirely due to electrons.

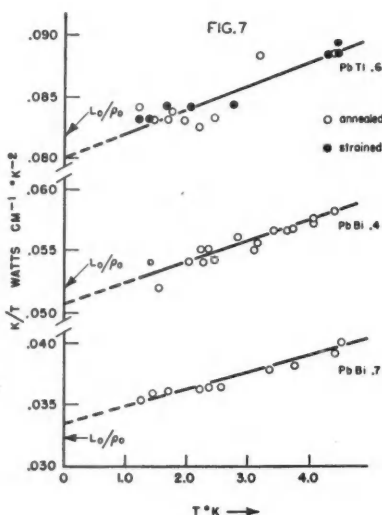


FIG. 7. K_n/T for three lead alloys.

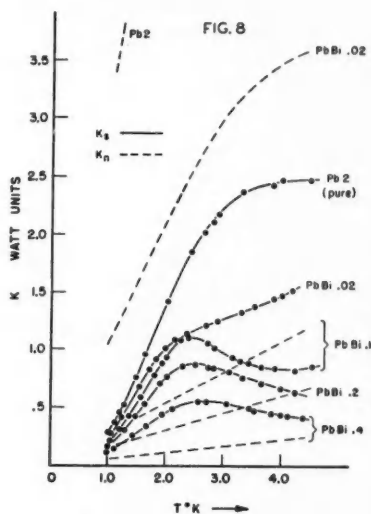


FIG. 8. K_s for some lead alloys.

The results for K_n are thus in reasonable qualitative agreement with theory. At sufficiently low temperatures L agrees closely with the classical value, which means that K_n must be predominantly electronic.

Turning now to K_s , which for the first series of Montgomery's specimens is plotted in Fig. 8, it becomes at once apparent that, whereas the K_n values are strongly dependent on impurity, the K_s values for all the alloys reach the same order of magnitude at low temperatures. Assuming that here K_s is mainly due to phonon conduction which has been freed from scatter by electrons, the result seems reasonable. The dominant phonon wavelength in lead at 1° K. is about 50 lattice spacings, and point imperfections are thus unlikely to be effective scattering centers.

The superconductor should therefore behave like a dielectric crystal and, taking θ_D for lead as 96° K., one should expect from Casimir's formula

$$K = 3.9 d T^3,$$

where d is the specimen diameter. For the specimens used by us ($d \sim 0.25$ cm.), K_s at 1° K. should be of the order of 1 watt but it is clear that the experimental values are all lower. This can be understood by the extra scattering effect due

to grain boundaries and dislocations. Analysis shows that the former factor alone cannot have been responsible and the latter required further investigation.

The assumption of predominant phonon conduction at low temperatures in a superconductor can thus be tested on three predictions:

1. K_s should become size dependent for dimensions below the phonon mean free path (~ 0.05 cm.) provided the specimen is free of strain.
2. K_s should be largely independent of the amount and type of impurity.
3. K_s should be strongly reduced by introduction of extended lattice imperfections by, say, cold work at room temperature.

The first test seems easy except for the difficulty of avoiding strain, which as predicted under (3), also would reduce K_s as, in fact, it does. The difficulty was overcome by Montgomery by making the specimen in the form of a cylindrical scroll of pure lead of 0.007 cm. diameter. This could be mounted between two cylindrical copper plugs in such a way as to be sufficiently strong mechanically. After annealing, the crystal size was about 0.2 cm., which means 30 times the diameter. The results are shown together with similar measurements on a single crystal of the same material of 0.2 cm. diameter in Fig. 9. As was to be expected, K_n is very similar at all temperatures for both specimens and so is K_s at higher temperatures. However, at 1° K., K_s of the scroll is five times smaller than K_s of the bulk material. Moreover, K_s varies as $T^{2.8}$, which

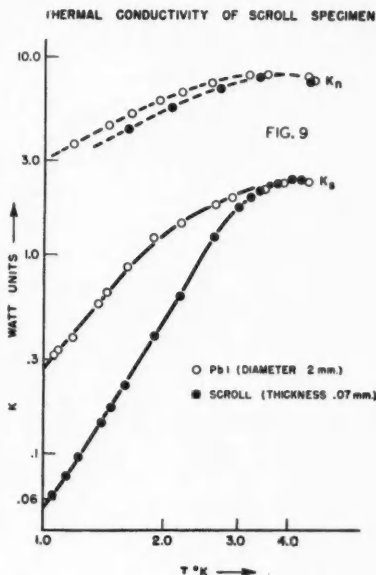


FIG. 9. K_s , K_n for scroll and bulk metal.

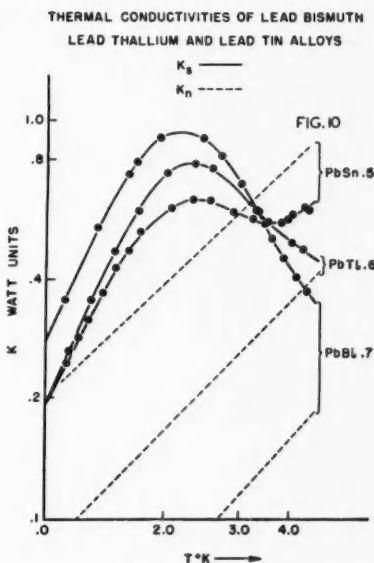
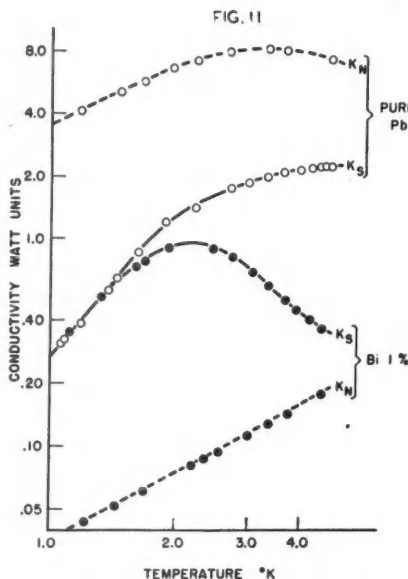
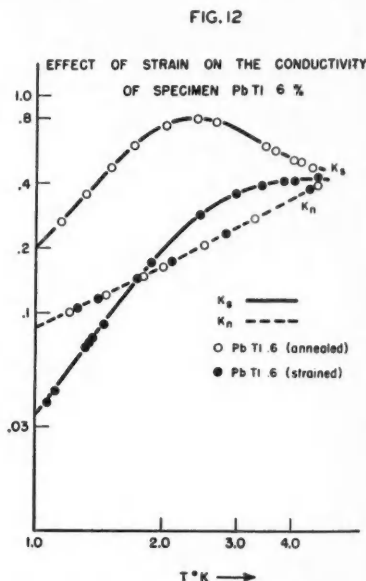


FIG. 10. Thermal conductivity of Pb Bi, Pb Tl, and Pb Sn alloys.

is close enough to the T^3 law to be expected for boundary scattering. The mean free path derived from this value is 0.014 cm., which is just twice that of the scroll thickness. Montgomery has recalculated Casimir's formula for the case of a flat plate and has shown that if the experimental result from the foil is used, the phonon mean free path for the bulk material of the foil derives as ~ 0.06 cm., a value to be expected from the observed grain size. Thus, one may conclude that the predicted size effect in K_s does actually exist.

The test of the second prediction is shown first in Fig. 10, which gives K_s values for the specimens Pb Sn 0.5%, Pb Ti 0.6%, and Pb Bi 0.7% which were mentioned earlier. Although the K_n values are widely divergent, the K_s values become similar at low temperatures. The 30% higher value of the Pb Bi 0.7% specimen is probably due to the fact that this is a single crystal whereas the other two specimens were polycrystalline. Even more striking is the insensitivity of K_s on the amount of impurity, which could be tested by comparing the single crystal Pb Bi 0.7% with a pure lead single crystal (Fig. 11). Although

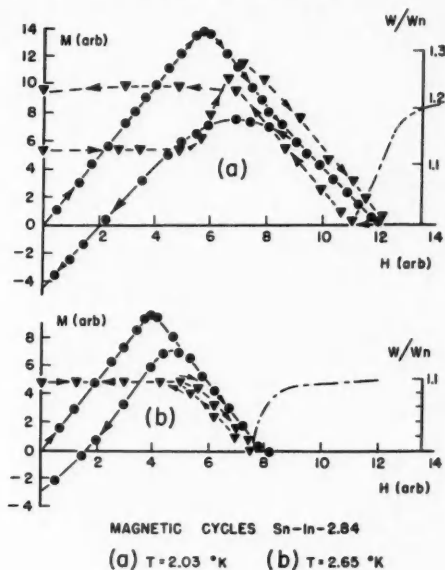
FIG. 11. Effect of impurity on K_s and K_n .FIG. 12. Effect of strain on K_s and K_n .

the K_n values at 1° K. for these specimens differ by a factor 100, their K_s values at the same temperature are identical. This result indicates clearly that while the electrons are strongly scattered by point imperfections, the phonons are completely unaffected by them.

On the other hand, we should expect the phonons to be scattered appreciably by large-scale lattice disturbances which would not necessarily scatter elec-

trons. An experiment to test the third prediction was therefore made by Montgomery in which the specimen Pb Tl 0.5% was measured before and after straining at room temperatures. The straining was done by bending the specimen *in situ* at room temperatures through an angle of $\sim 30^\circ$ and re-straightening it, several times. The results of this work are shown in Fig. 12. K_n has not changed at all with straining, but K_s has undergone a decrease to one sixth of its original value. Also its temperature dependence has changed from $T^{2.3}$ to $T^{2.7}$. Here no point imperfections are introduced and therefore the electrons are not scattered by the strain produced by cold work. The phonons, whose wavelength is much nearer to the order of magnitude of the extended lattice imperfections, are strongly scattered. These imperfections may have been dislocations, or dislocations which have migrated into an ordered pattern, or even recrystallization. The grain size determination indeed suggested this last possibility. On the other hand, there was no clear correlation in the values of K_s obtained in this work with the grain size.

The possibility of scattering due to dislocations forming into a mosaic structure was also apparent in the investigation on single crystals of the series Sn-In, undertaken recently by Shiffman (12); but a detailed discussion of this work, as indeed of many aspects of Montgomery's experiments, must be left to the full publications by these authors.



—●— Magnetic Moment
 - - - - - Thermal Resistivity Ratio
 - - - - - Electrical Resistance

FIG. 13. Magnetic cycles.

Only one aspect of the work on tin-indium should be mentioned and this is the investigation of the increase observed in the thermal conductivity of the specimen in the intermediate state. Shiffman has measured on the same specimen with transverse magnetization (1) the heat resistance, (2) the magnetic induction, and (3) the electrical resistance. The results on a specimen containing 2.84% of indium are given for two temperatures in Fig. 13. The onset of electrical resistance and the change of induction are much the same, but the pattern of the heat conductivity in the intermediate state is strongly affected by temperature. Whereas at the higher temperature (2.65°K.) there is hardly any hysteresis and certainly no pronounced maximum in W , a strong maximum has developed at 2.03°K. This is in good agreement with our earlier work on lead at very low temperatures in which the relative size of the maximum had been found to increase very much as phonon conduction became predominant.

Since phonon conduction is the only notable contribution to K_s in this region, it is clear that any appreciable reduction in K_s must be due to a scattering of phonons. This is further emphasized by a comparison of the temperature dependences of the percentage of frozen-in flux, as revealed by the induction measurements, and of the heat resistance maximum. Fig. 14 explains schematically the choice of quantities used in our comparison: $(W_B - W_L)/(W_S - W_N)$, the relative height of the maximum, and $(W_F - W_S)/(W_S - W_N)$, the percentage of thermal conductivity hysteresis when the field

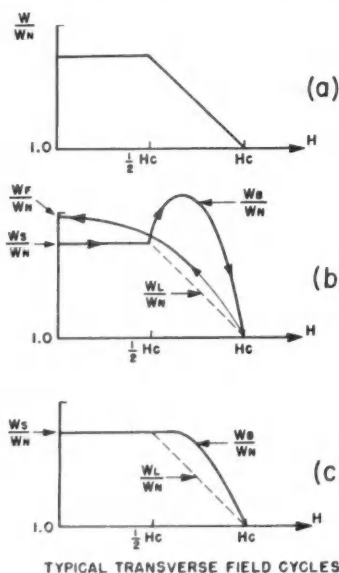


FIG. 14. Typical transverse field cycles.

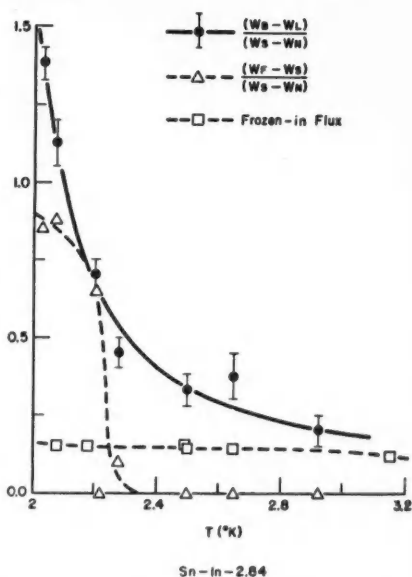


FIG. 15. Temperature dependence of heat resistance maximum and frozen-in flux.

was reduced to zero. The results, shown for the same specimen, are plotted against the temperature in Fig. 15. The percentage of frozen-in flux is practically temperature independent, while the height of the heat resistance maximum increases enormously on cooling. The thermal conductivity hysteresis, while rather more erratic in this particular specimen, follows roughly the trend of the maximum. This comparison shows beyond doubt that the appearance of the maximum at low temperatures cannot be due to the geometrical pattern of the intermediate state, since this remains unchanged as the temperature is lowered, but to a temperature dependent feature of the conduction process within this pattern.

In conclusion, I like to reiterate that this report, owing to its one-sidedness, must not be taken as a general survey of the field at this stage. It merely means to illustrate some of the present trends and in particular the use of the phenomenon of superconductivity as a useful tool in the study of metals.

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DISCUSSION

For discussion of this paper, see page 1331.

CONDUCTIVITY OF METALS AT LOW TEMPERATURES¹

By G. K. WHITE²

As an addendum to Dr. Mendelssohn's contribution which has paid particular attention to superconductors, I would like to review very briefly some work done recently in collaboration with Dr. Woods at the N.R.C., and in Sydney with Dr. Klemens and Messrs. Kemp and Sreedhar (now at Ohio State). This has dealt largely with non-superconducting metals and one wishes to emphasize both the uniformity and the diversity of the information obtained and lay the problem anew before the theoreticians.

Firstly, in the alkali metals we observe (MacDonald, White, and Woods 1956) that the "ideal" electrical and thermal resistivities ρ_i and W_i have the temperature dependences, for $T \leq \theta/10$, expected of monovalent metals; viz. $\rho_i \propto T^m$ and $W_i \propto T^n$ with $m \simeq 5.0$ and $n \simeq 2.0$, with one notable exception. In sodium very careful observation by Woods (1956) showed that for $T < 8^\circ \text{K}$, $m \simeq 6.0$. As far as the magnitude of these resistivities is concerned, comparison of the values for $T < \theta/10$ with high temperature values ($T \sim \theta$ where $\rho_i \propto T$, and $W_i = W_\infty$ is sensibly constant) shows that* experimentally W_i is about four times smaller than the Sondheimer and Klemens solutions of the transport equation would predict; on the other hand ρ_i is generally several times larger, except for sodium which follows the Bloch-Grüneisen law tolerably well down to 8°K . These discrepancies are reflected in the comparison of the two resistivities at low temperatures, where the existing theory would predict (following Klemens and Ziman) that

$$\rho_i \theta^2 / W_i T^3 \simeq 1.9 \times 10^{-7} \text{ watt-ohm/deg.}^2$$

Experimental values range from 6×10^{-7} for Na to about 30×10^{-7} for Li, Rb, and Cs.

For the other "simple" metals Cu, Ag, and Au (see for example the review by Klemens (1956) for experimental data and theoretical discussion of the transport equation), ρ_i follows the Bloch-Grüneisen function fairly well, but W_i is again about four times smaller than the theoretical prediction; for Ag and Cu small departures from Matthiessen's rule in ρ_i and W_i were observed and values of the index n for W_i appeared to be somewhat greater than the expected value 2.0.

Incidentally we (MacDonald, White, and Woods 1956) have suggested that an empirical function $W_i/W_\infty = 2(T/\theta)^2 J_3(\theta/T)$ might be expected to fit the thermal resistivity data over a restricted low temperature range—the range where a single scattering of an electron by a phonon can change the energy sufficiently to restore equilibrium but the momentum change is very small—

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10–14, 1956.

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*The values of θ used are the values of θ_D determined from specific heat data for the temperature region in the vicinity of θ_D .

and this function seems to agree with the observed ratio W_i/W_∞ to within $\pm 30\%$ over a surprisingly wide temperature range from $T \sim \theta$ to $T \leq \theta/10$, for most pure metallic elements. Therefore the function (tabulated by MacDonald and Towle 1956) combined with the Wiedemann-Franz law seems useful for predicting thermal conductivities from isolated experimental values of the electrical resistance obtained at low and high temperatures.

Detailed work on the transition elements is still incomplete, but in a small family of Pd (Kemp *et al.* 1955), Cr (Kemp *et al.* 1956*b*), Fe and Ni (Kemp *et al.* 1956*a*) it was observed that, for $T \leq \theta/10$, $W_i \propto T^2$ and $\rho_i \propto T^3$, suggesting (following Mott (1936) and Wilson (1938)) that s - d band transitions are still important at these temperatures. Other elements, e.g. Pt and W, have the index $m \simeq 4$; and for V, Nb, Ta at temperatures $< \theta/10$, $3.5 < m < 4.0$. For Re, Rh, Ir (White and Woods 1956*b*) experiments show that $4.5 < m < 5.0$ and that the thermal resistivity index n is closer to 3 than to 2. Do these latter results suggest that s - d transitions are becoming "frozen-out" in this temperature range? However, it seems very doubtful that the study of "ideal" resistivities is a good method of investigating the band structure of transition metals, but perhaps data on electrical resistance arising from electron-electron interactions may yield more direct information about effective electron masses. Apparently only in Pt and Pd (see contribution by Mendelssohn) have T^2 terms in the electrical resistance (suggested by Baber (1937) as due to electron-electron interactions) been observed at very low temperatures; but if other transition metals can be obtained in a sufficiently pure and suitable geometrical form, this study may prove of some value.

With regard to lattice thermal conductivity K_θ , the work on copper and silver and some of their alloys (see Klemens (1956) for review) leads us to believe that the conduction electrons interact with lattice waves of all polarizations in these elements. We should like to extend this study to sodium and potassium, but our success has been very limited up till now because of the difficulty of getting sufficient impurities into solid solution in these elements to reduce the electronic conduction and thereby make the lattice component measurable.

In conclusion, another series of experiments underway at the moment is that on heat conduction in the solid inert gases. Results on argon (White and Woods 1956*a*) show that the magnitude of the conductivity at temperatures $T > \theta/10$, where phonon-phonon interaction seems to be the dominant mechanism limiting the conductivity, agrees with that predicted by Leibfried and Schlömann (1954) and Dugdale and MacDonald (1955) on simple central force models, relating conductivity to the elastic constants, velocity of sound, etc. As far as can be seen from the lattice conductivity data on silver and copper, the magnitude of K_θ in this region where $K_\theta \propto T^{-1}$ is somewhat lower, but not markedly so, than that predicted by these authors.

The accompanying figures illustrate the temperature dependence of the resistivity due to scattering of electrons by thermal vibrations in the case of some representative alkali and transition metals.

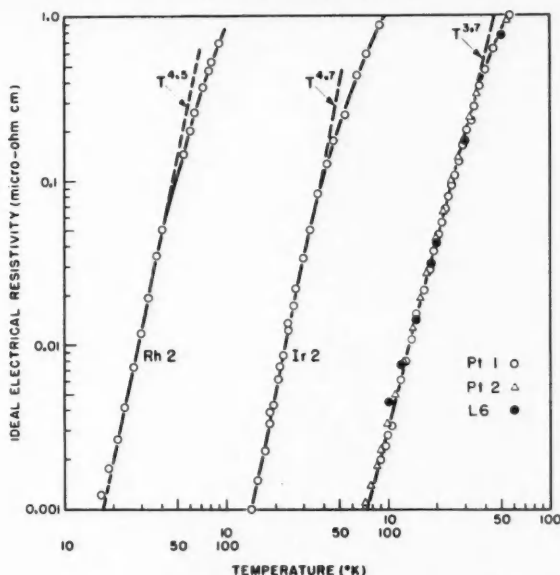


FIG. 3. Ideal electrical resistivity of rhodium, iridium, and platinum at low temperatures.

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DISCUSSION OF THE PAPERS OF MENDELSSOHN AND WHITE

Ziman: The experiments of Graham at Cambridge on superconductive tin have found that the curve tends towards $K \sim T^4$, so that $l \sim T$. This would suggest that the scattering of phonons varies proportionately to the wavelength, and this in turn suggests a possible explanation.

Some years ago Nabarro found that a screw dislocation would flutter in the field of a long acoustic vibration, producing a scattering width proportional to λ . Calculations show that this would provide scattering of the right order of magnitude.

Mendelssohn: In all the substances that we have examined down to 0.2°K . the conductivity has never decreased more rapidly than T^3 .

Ziman: Adjustment of parameters in the theory might give any variation between T^3 and T^4 . An important point is that grain boundaries are not enough to cause the scattering found in your experiments, so that some additional source is required, and the necessary density of dislocations is reasonable.

Bloembergen: Have any measurements been made of the attenuation of ultrasonic waves, thus getting more directly the scattering of phonons?

Fröhlich: Yes. In experiments at the Bell Telephone Company's laboratories the attenuation was found to be much lower in the superconducting state.

Klemens: Ultrasonic waves of almost macroscopic wavelength would not necessarily have the same cross-section as the much shorter waves giving rise to thermal conductivity.

Mendelssohn: The temperature dependence of ρ in rhodium ($\sim T^{4.5}$) in the experiment described by Dr. White is very different from that we observed in Oxford ($\sim T^{1.6}$). This would suggest the importance of using unstrained zone-refined specimens, taking the utmost care to avoid cold work. If this could be done, I don't think that very low temperatures would be needed to find the significant behavior: $4\text{--}10^\circ\text{K}$. should be an ideal range.

Pines: We should look for an electron-electron interaction in W as well as ρ ; corresponding to the term proportional to T^2 in ρ there should be a term proportional to T in W .

White: This suggestion has also been made by Klemens, but at present it is not possible to measure W accurately enough.

Joffé: Dr. Mendelssohn may be interested to know that we have developed a method of isothermal zone-refining; by making use of the Peltier heat we avoid the need of a temperature gradient.

Gorter: Ramachandrachari and de Nobel have recently been carrying out measurements on the heat conductivity at low temperatures of a series of silver alloys containing between 0.1 and 1 at. % of Mn—one alloy with 0.24 at. % of In also being studied—and of a series of steels.

The results all show an anomaly of a few per cent in the conductivity around 2° or 2.5°K ., in the sense that at the lower temperatures the thermal conductivity is increased by a few per cent with respect to what an extrapolation from higher temperatures would lead one to expect. The anomaly has been observed by three kinds of thermometers and also occurs if, by a large magnetic field, the conductivity is increased by some 20%, but it was not found in pure silver. Thus, if the effect is real, it must be due to the lattice component of the conductivity and Ramachandrachari, in his thesis, places it in parallel with the well-known anomaly found by Wilkinson, Wilks, and Berman for quartz glass. This anomaly has been explained by Klemens as due to a peak in the contribution of longitudinal phonons and Ramachandrachari suggests that the present anomaly might be due to a peak in the transverse phonon contribution to the thermal conductivity of the alloy. As

a matter of fact the possibility of such an effect was already indicated by Klemens in his chapter in the *Handbuch der Physik*, §20, case (c).

If the anomaly is ignored one may describe the thermal conductivity by

$$\kappa \approx L_0 T / \rho_0 + T^2 / 400,$$

L_0 being the Lorenz factor and ρ_0 the electrical residual resistance. The magnitude of the second term, which represents the lattice contribution, confirms the correctness of the Makinson scheme for the scattering of phonons by the conduction electrons. At liquid hydrogen temperatures the lattice contribution has decreased because of scattering by impurities and lattice defects.

Following **Gorter's** remarks, **Frederikse** asked whether the anomaly could be due to an inadequacy in the temperature scale (cf. the apparent anomaly observed by Keesom and Pearlman in the specific heat of silver). **Gorter** replied that the corrected temperature scale had been used. **Mendelssohn** said that similar anomalies had been found in Sn-In and also in Ta. **Klemens** said that if this effect were indeed due to loose coupling between the transverse and longitudinal phonons at the lowest temperatures, then the interaction of electrons with transverse waves must be weaker than with longitudinal waves, although of a similar magnitude (cf. Gorter's remark in the discussion after Bardeen's paper).

ON THE MAGNITUDE OF THE CONTRIBUTION OF A CIRCULATION EFFECT TO THE THERMAL CONDUCTIVITY OF A SUPER-CONDUCTOR¹

BY C. J. GORTER²

The anomalously large heat transport in liquid helium II is, on the basis of the two-fluid model, generally attributed to an internal circulation of normal and superfluid matter.

The analogy between superconductivity and the superfluidity in helium II has induced many people to ponder about the consequences of a similar circulation in superconductors; cf. the discussions of Ginsburg, Mendelssohn, Olsen, and Klemens. The conclusion reached seems to be that the contribution due to a circulation effect is several orders of magnitude smaller than the normal thermal conduction by the normal fraction of the electrons. It is the purpose of the present remarks to stress that the two-fluid model is not well enough defined to make this conclusion stringent.

Let us first consider the more familiar situation of liquid helium, using this as a starting point for the discussion of a superconductor. Leaving aside accelerations and mutual friction one may write the equations of motion for the superfluid and the normal fluid contained in a unit of volume

$$(1) \quad (1-x) \text{ grad } p = x(1-x)\rho S^* \text{ grad } T,$$

$$(2) \quad x \text{ grad } p = -x(1-x)\rho S^* \text{ grad } T - f_P v_n$$

where x and $(1-x)$ are the relative concentrations of normal fluid and superfluid, S^* is either $(\partial S/\partial x)_T$ or S/x , v_n is the velocity of the normal fluid, while f_P is the coefficient of the Poiseuille friction in the slit or capillary concerned.

From (1) we get for the fountain effect

$$(3) \quad \text{grad } p = \rho x S^* \text{ grad } T$$

and from (1) and (2) for the normal fluid velocity

$$(4) \quad v_n = -(\rho x S^*/f_P) \text{ grad } T.$$

Substituting this in the expression for the transport of energy by circulation

$$(5) \quad w = v_n \rho x S^* T$$

we get

$$(6) \quad w_{\text{circ}} = -(\rho^2 x^2 S^{*2} T/f_P) \text{ grad } T.$$

The expression for the free energy of Gorter and Casimir

$$(7) \quad F = xU_0 - \frac{1}{2}x^{\frac{1}{2}}\gamma T^2$$

seems to supply us with expressions for $(\partial S/\partial x)_T$ and S/x . They differ by a factor 2, but since we shall only be concerned with orders of magnitude we provisionally accept the second one which, admitting

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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$$(8) \quad x = T^4/T_c^4,$$

gives

$$(9) \quad S^* = \gamma T_c^2/T.$$

If we now replace $\text{grad } p$ by neF , where F is the electric field and ne the electronic charge density, we run immediately into difficulties with the analogue of the fountain effect, for which we get

$$(10) \quad F = (\rho x S^*/ne) \text{ grad } T = (\rho \gamma T^3/ne T_c^2) \text{ grad } T,$$

which leads to a thermoelectric force of the order of 10^{-7} volts/degree. There has never been found a trace of such a thermoelectric force, and the easiest way to get rid of it is to suppose that the diffusion force on the superconductive electrons is compensated by some non-electric force preventing their compression and to put the left-hand sides of (2) and (1) equal to zero. As a consequence the right-hand sides of (4) and (6) have to be multiplied by $(1-x)$, and introducing then for f_p : $n^2 e^2 x / \sigma$, where σ is the electrical conductivity of the normal phase, one gets

$$(11) \quad \begin{aligned} w_{\text{elre}} &= -[\rho^2 x (1-x) S^{*2} T \sigma / n^2 e^2] \text{ grad } T \\ &= -(\rho^2 \gamma^2 \sigma T^3 / n^2 e^2) (1 - T^4/T_c^4) \text{ grad } T. \end{aligned}$$

We shall compare this energy current with the heat current w_n in the normal phase due to the electrons and evaluated from the electrical conductivity with the aid of the Lorenz parameter $L = (\pi^2/3)(k/e)$, where k is Boltzmann's constant and e the charge of the electron. Then

$$(12) \quad w_n = -(\pi^2 k^2 \sigma T / 3 e^2) \text{ grad } T$$

and

$$(13) \quad w_{\text{elre}}/w_n = (3 \rho^2 \gamma^2 T^2 / \pi^2 n^2 k^2) (1 - T^4/T_c^4).$$

Considering that $\rho \gamma T_c / nk \approx 10^{-3}$, the conclusion that w_{elre} is negligible seems to be confirmed.

However, the acceptance of (9) may be criticized since it has tacitly assumed that all the conduction electrons may be divided into superconductive and normal ones, while it might be argued that this distinction should only be applied to electrons in or near to the Fermi tail. This would multiply S^* by a factor $nk/\rho \gamma T$, leading to the conclusion that $w_{\text{elre}} \approx 10^{-1} w_n$.

The application of this factor means that the heat to be supplied in order to transform one superconductive electron into one normal electron is of the order of kT_c . This can be illustrated by a simple order-of-magnitude argument. When the energy transported by circulation is w_{elre} , the energy available per unit volume to be transformed into Joule heat is of the order $|w_{\text{elre}} \text{ grad } T|/T$. If this is equalized to the expression $j^2/\sigma = (n_e e v)^2/\sigma$, admitting $w_{\text{elre}} = n_e v k T_c$, one obtains

$$(14) \quad w_{\text{elre}} \approx -(k^2 T_c^2 \sigma / e^2 T) \text{ grad } T,$$

which is of the same order as w_n .

So it seems quite possible that w_{elre} should not be neglected, and one might look for effects that could be influenced by it. The anomalous heat conduction of Pb might perhaps be such an effect.

PHENOMENOLOGICAL ASPECTS OF THE RESISTIVITY OF PURE METALS¹

By G. BORELIUS²

Our understanding of the temperature dependence of the resistivity of pure metals depends very much upon our understanding of the thermal motion of the crystal lattice. Thus before entering upon some phenomenological aspects of the resistivity, I shall have to present briefly some ideas concerning the thermal motion.

Fluctuation considerations (1) have led to the relationship

$$[1] \quad \Delta U / \Delta V = \frac{3}{2} \alpha$$

between an increase in potential energy U due to increased fluctuations, the corresponding increase in volume V , and the pressure parameter α occurring in the equation

$$[2] \quad (\Delta p + \alpha)(\Delta V + \beta) = \alpha \beta$$

describing the change of molar volume ΔV with a change of pressure Δp .

The second parameter in [2], β , is the compressible part of the molar volume V ; this follows from the fact that if Δp increases infinitely $-\Delta V$ approaches the value β . From [1] and [2] we derive

$$[3] \quad \beta / V = \alpha \kappa,$$

where κ is the compressibility.

As a special case for low temperatures, where the potential energy is half of the total thermal energy, equation [1] gives proportionality between heat capacity and volume expansion, i.e. the first Grüneisen law. Equation [3] may be transformed into

$$[3'] \quad \beta / V = \frac{2}{3} (\Delta U / \Delta V) \kappa = 1/3 \gamma,$$

where γ is the number obtained by combination of heat capacity, thermal expansion, and compressibility, found by Grüneisen to be of the order of 1 to 3. Equation [3] thus gives a simple interpretation of this second law of Grüneisen. It simply means that the compressible part of the volume is between 35 and 15% of the total volume, with higher values for the body-centered and lower values for the face-centered cubic metals.

For the present problem concerning the resistivity, the potential energy U is of special interest. We can obtain U as a difference between the total thermal energy and the kinetic energy from the equation

$$[4] \quad U = \int_0^T C dT - \frac{3}{2} RT \times D(T/\theta).$$

Here C is the observed heat capacity per mole, R the gas constant, and

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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$D(T/\theta)$ the Debye function going from 0 to 1 with increasing temperature T , the characteristic temperature θ being taken from the heat capacity at low temperatures. We thus have assumed the kinetic energy to approach at high temperatures the classical value $3RT/2$; that is, we have excluded rotational degrees of freedom for the atoms of the metal. For the liquid metal we add to [4] the total heat of fusion, which is thus assumed to be entirely made up of potential energy.

The significance of U , as obtained from [4], is shown in Fig. 1 by a plot for Pb of U against the volume thermal expansion, which gives a slightly bent curve going continuously through the solid and liquid states. Pb is the metal

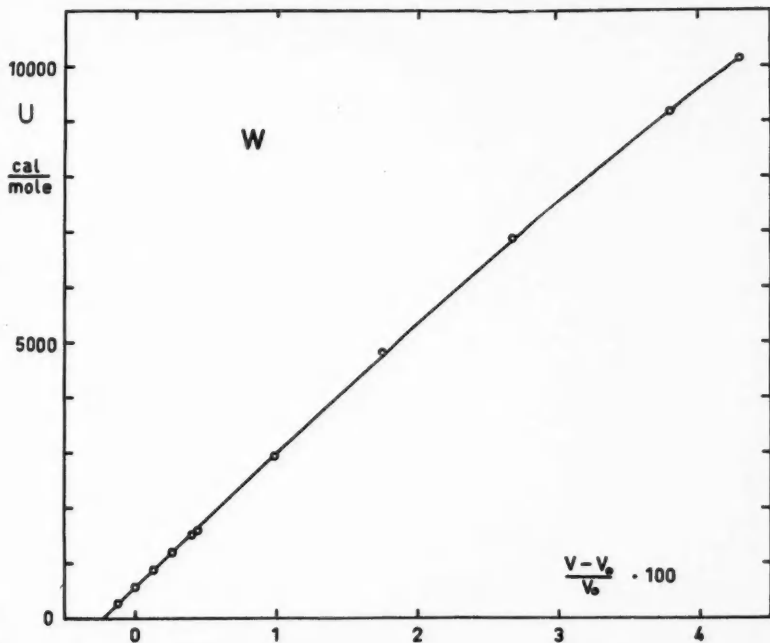


FIG. 1.

for which we have the most accurate measurements in the liquid state. Within the limits of error we have continuous curves also for the other close-packed face-centered cubic metals Cu, Ag, Au, and Al (2). According to equation [1] the bending of the curves means that the pressure parameter α decreases with increasing volume.

If, as assumed, U is a measure of the potential energy stored up by density fluctuations, it is also a measure of the disorder in the lattice and may be connected with the scattering of the conduction electrons. It has been of interest, therefore, to study plots of resistivity versus potential energy (2).

Such plots are shown in Fig. 2 for five face-centered metals, and in Fig. 3 for three body-centered metals. The ordinates are the resistances relative to the resistances at 0°C .

From the zero points, corresponding to 0°K ., the curves seem to start approximately linearly. Exact linearity would mean proportionality between resistance and potential energy (and also total thermal energy). It should be of interest to learn from suitable experiments whether this proportionality is perhaps more exact than the adaption to a T^4 or a T^5 -law. In a range of temperature on both sides of $T = \theta$ the curve turns over to about half the initial slope and is linear over a wide range. The extension of this line gives an intercept on the energy axis which we call U_z . The linear part may thus be written

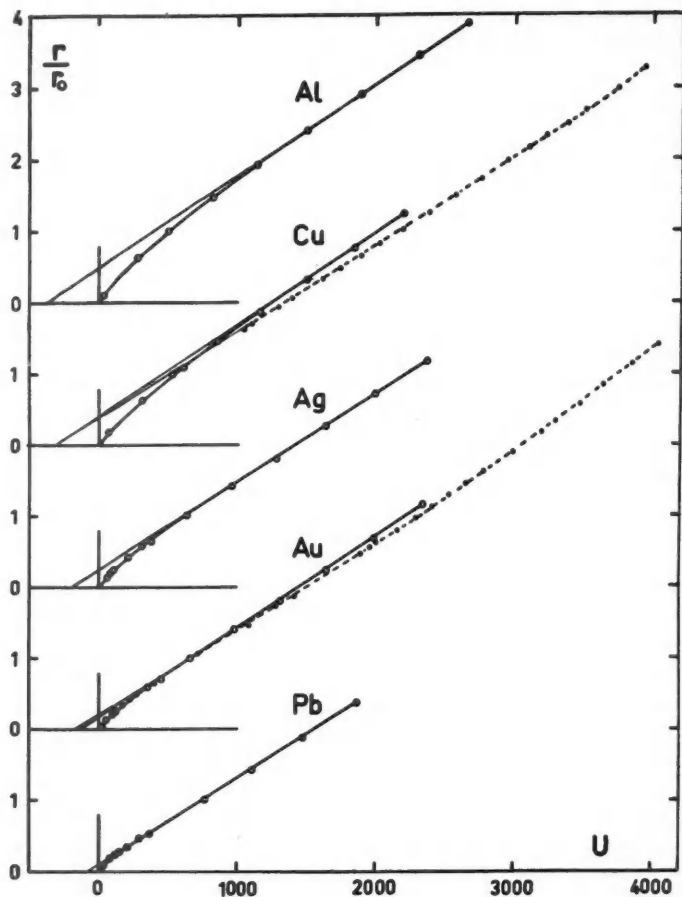


FIG. 2.

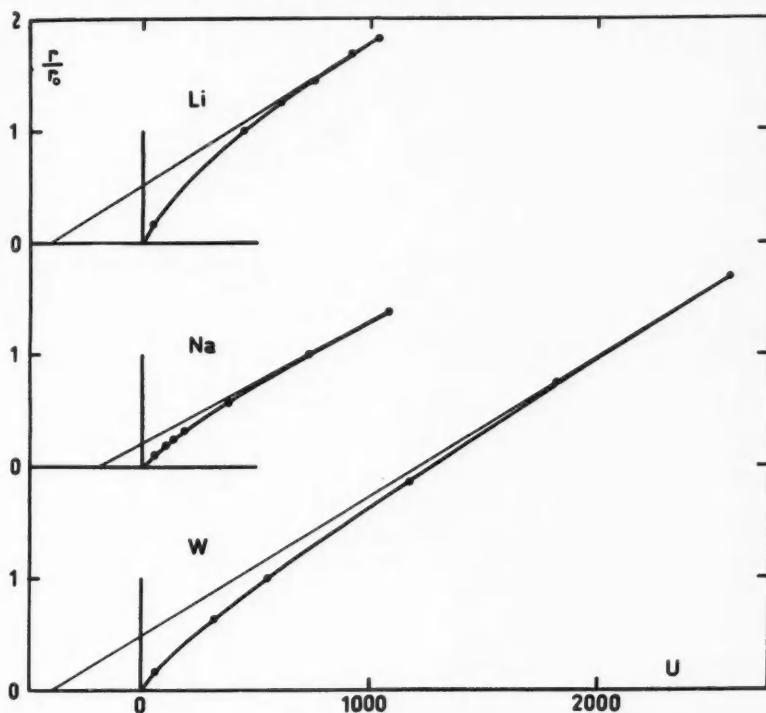


FIG. 3.

$$[5] \quad \rho/\rho_0 = \text{const.} \times (U_z + U).$$

U_z increases with increasing characteristic temperature θ and can be identified as the potential half of the zero-point energy:

$$[6] \quad U_z = \frac{3}{2} N h \bar{\nu} / 2,$$

where N is Avogadro's number, h Planck's constant, and $\bar{\nu}$ the mean value of the lattice frequencies at the zero point. $\bar{\nu}$ can be compared with the limit in frequency ν_D obtained from θ by the equation

$$[7] \quad \theta = h \nu_D / k.$$

The experimental values of $\bar{\nu}/\nu_D$ are shown in Table I. The mean value is 0.67. The Debye approximation gives 0.75, while other more detailed calculations give somewhat lower values.

If this identification of U_z with potential zero-point energy is correct, the problem of the temperature dependence of the resistivity is essentially related to the problem of how the zero-point energy, which does not of itself scatter the electrons, is gradually brought into cooperation with the scattering thermal energy.

TABLE I

	U_n , cal./mole	θ	\bar{v}/v_D
Al	390	398	0.66
Cu	280	325	0.58
Ag	190	215	0.59
Au	170	190	0.60
Pb	75	88	0.57
Li	400	363	0.74
Na	190	159	0.80
W	390	310	0.84

Another question that arises from our point of view is whether there is a similar continuity between the solid and liquid states for the relationship between resistivity and potential energy as for the relationship between thermal volume expansion and potential energy. As shown by Fig. 4, the

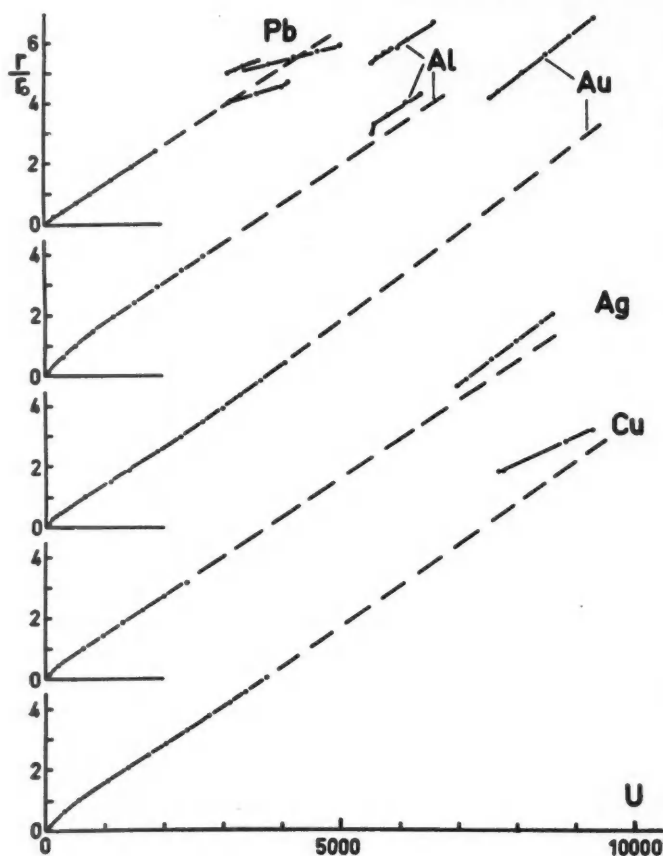


FIG. 4.

available experimental results are too uncertain to give an answer to this question. For Cu and Ag the experimental values of resistivity in the liquid metals are rather near to the extrapolated ones. For Au the discrepancy is rather pronounced. For Al the results of one observer are near to the extrapolated values, while those of another give a discrepancy of the same order as for Au. For Pb there are again diverging results from different investigations. New measurements with a detailed study of the influence of possible contaminations from the container and the atmosphere would be very welcome.

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DISCUSSION OF BORELIUS'S PAPER

Pines: We should be grateful to Professor Borelius for reminding us of the need to look at liquid metals, and especially the theory of their conductivity. For example, the simple concept of Umklapp processes depends on a regular lattice structure; and again, transverse waves depend upon rigidity. Yet we do not get an enormously different behavior for the conductivity on passing to the liquid from the solid.

Mott: At high temperatures the resistance can well be calculated from an Einstein model. The analyses into phonons, Umklapp processes, etc. are not important. So perhaps the small change on melting is not surprising.

Aigrain: We have in Paris just embarked upon the measurement of the Hall effect and the resistivity in mercury. As yet the work is only in its preliminary stage, and we are finding quite a number of difficulties—for example, the mercury tends to move away when it is magnetized; thus early results give us 10 electrons for each atom—a somewhat excessive number!

Mott: The mean free path in the liquid is still quite a lot bigger than the short-range order distance.

Joffé: We have done some work in Russia upon the resistance either side of the solid-liquid transition, both in metals and semiconductors. The main result is that it is the *short-range* order and the *localized* chemical bonds that are the dominant factors in determining resistance.

Mott: One would like to know how far the description of a liquid as composed of very small grains of solid is adequate for discussing resistance.

MacDonald: I wonder whether the resistance change on melting cannot be rather simply accounted for as follows. As we approach the melting point in sodium, we can observe rather clearly the extra increase in resistance due to the thermal formation of lattice defects ("vacancies" for simplicity). I believe I'm right in saying that one observes about 5% increase in resistance just before the (very sharp) melting point; this increase is due to a number of vacancies of the order of 1/10% or perhaps somewhat less. In addition, however, it appears that one may say that about 3% of "vacancies" occur on melting proper. Therefore if we just take these figures naively at their face value we should then expect about 100% total increase of resistance on melting, which is certainly of the right order of magnitude.

HEAT TRANSFER IN SEMICONDUCTORS¹

By A. F. JOFFÉ²

Our main interest in heat conductivity arose from the task of improving the efficiency of semiconducting thermoelectric couples. The efficiency of any thermoelectric device depends on the value of $Z = \alpha^2 \sigma / \kappa$; α = the thermoelectric power, σ = the electrical, κ = the thermal conductivity. We thus had to investigate both the electric and the thermal behavior in the temperature range between -100° and $+500^\circ$ C.

For most of the materials we had to deal with, this meant the neighborhood of the Debye temperature. We had to establish some rules allowing us to estimate the value of heat conductivity and had to know the influence of the temperature on the conductivity.

According to the general belief one would expect that:

1. The actual value of phonon heat conductivity κ_{ph} cannot be derived from theoretical considerations.

2. The thermal resistivity beyond the Debye temperature would be proportional to the absolute temperature T .

3. The total heat conductivity κ of a semiconductor would be composed additively of a phonon term and an electronic one, the last following the Wiedemann-Franz ratio:

$$(1) \quad \kappa = \kappa_{ph} + L\sigma.$$

In order to be able to try hundreds of samples we used an apparatus which proved to be better than we would expect.

The flow of heat from one copper block to a second small block through the specimen was measured in intervals of 15-30 sec. Simultaneously the temperature difference between the two blocks was measured (Fig. 1).

Eliminating some obvious sources of error we get the value of conductivity with an accuracy of 2 to 3%. The measurement took less than five minutes.

On looking at the thermal conductivity of non-metals in the periodic system of elements we easily discover a tendency for the conductivity to decrease with rising atomic weight. In fact for the first two horizontal rows κ has a value of several tenths of one cal./deg.sec.cm., while it decreases to a few hundredths for the elements of the middle part of the chart and to some thousandths in the lower part of the table. Such exceptions as sulphur may be explained by the ring-shaped structure of the lattice, consisting of six or eight atoms.

An insight into the rules governing the heat conductivity is given by Fig. 2, where $\log \kappa_{ph}$ ($T = 300$) is plotted against $\log \bar{A}$, \bar{A} being the mean atomic weight of the elements composing the sample. Most of the data used follow from our experimental work; others are taken from tables of constants.

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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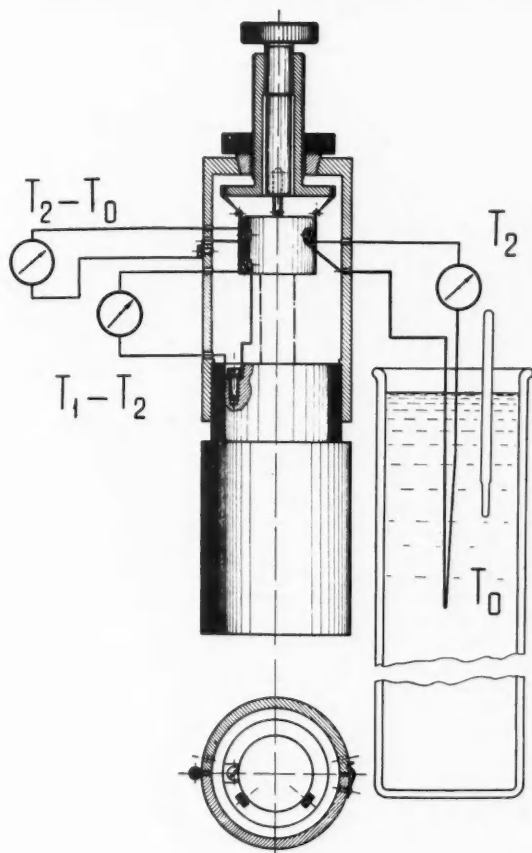


FIG. 1.

Substances with analogous lattice and similar chemical bond are connected by full lines.

The following rules may be deduced:

1. For substances with similar structures κ_{ph} decreases as \bar{A} increases.
2. The phonon conductivity decreases with increase of the proportion of the ionic part of the chemical bond; in fact κ_{ph} decreases along the following sequence: the elements of Group IV, compounds of elements of Groups III and V, then II with VI, and finally I with VII.
3. Ionic crystals with ions of equal masses have higher conductivities than crystals with ions of different masses. This latter rule has been stated already many years ago by Eucken.

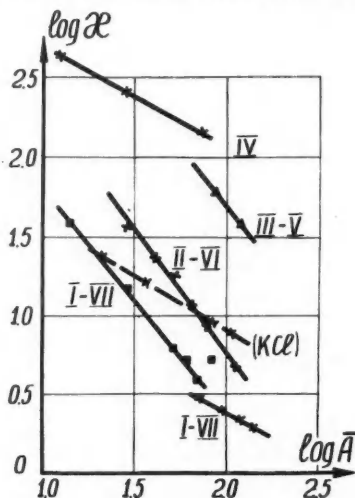


FIG. 2.

We did not succeed in finding any difference between the oxides of the left side of the second group and of the right side, in spite of a different ratio of ionic and valence forces in these two cases.

Simultaneously with a decrease of heat conductivity κ the increase of the atomic weight \bar{A} causes an increase of the mobility u of electric charges. The ratio u/κ , which is essential for the efficiency of a thermocouple, increases with the atomic weight.

Our next concern has been the temperature dependence of the phonon conductivity.

The hypothesis that at temperatures near or above the Debye temperature the heat resistance may become proportional to the number of phonons present leads to the formula:

$$(2) \quad \left(\frac{1}{\kappa_{ph}} \right)_{T=300^\circ K.} = \frac{C}{v} \left(T - \frac{\theta}{3} + \frac{\theta}{24} \frac{\theta}{T} - \dots \right) \cong \frac{C}{v} \left(T - \frac{\theta}{3} \right);$$

here C depends on the anharmonicity of cohesive forces, on the frequency of atomic oscillations, and on the crystal structure, while v is the sound velocity. Plotting $1/\kappa_{ph}$ against T , a straight line will be found crossing the abscissa at $T = 0.30\theta$ instead of $T = 0$. Extrapolating the slope at temperature $T = 0.50\theta$ to lower temperatures one finds it crosses the abscissa at about 0.2θ .

To prove these conclusions we made precise measurements on pure crystals of KCl and KBr. Both are known to follow closely Debye's formula for specific heat. The plot may be represented in both cases by straight lines starting at 0.3θ and 0.2θ . The measured points coincide practically with the computed lines (Fig. 3).

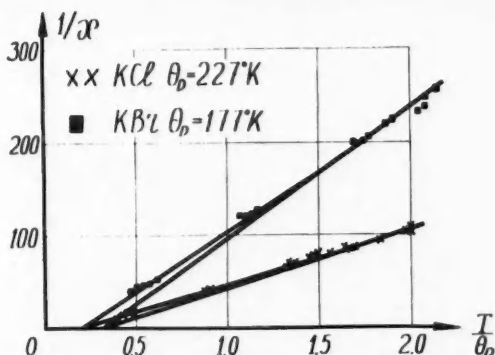


FIG. 3.

If one uses a logarithmical plot the relation between $1/\kappa_{ph}$ and T is approximated by $1/\kappa \sim T^n$. According to formula (2) n depends on T/θ . For instance:

at $T = 0.5\theta$,	$n = 1.33$;
at $T = 1.0\theta$,	$n = 1.20$;
at $T = 2.0\theta$,	$n = 1.09$;
at $T = 3.0\theta$,	$n = 1.05$.

I remember on this occasion that Drs. White and Woods got for Ge at $T \cong 0.5\theta$: $1/\kappa \sim T^{1.3}$.

The validity of the formula (2) is often obscured by impurities introducing additional scattering. The line $1/\kappa = f(T)$ becomes then shifted to the left. It is shown in Fig. 4 for PbTe with 5×10^{17} and 6.2×10^{18} free electrons cm^{-3} .

The role of impurities becomes more pronounced in the low temperature range. An illustration of the influence of impurities may be seen in Fig. 5,

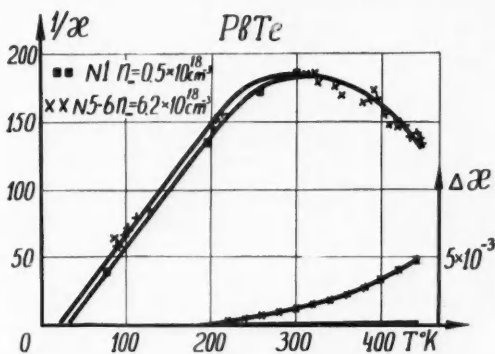


FIG. 4.

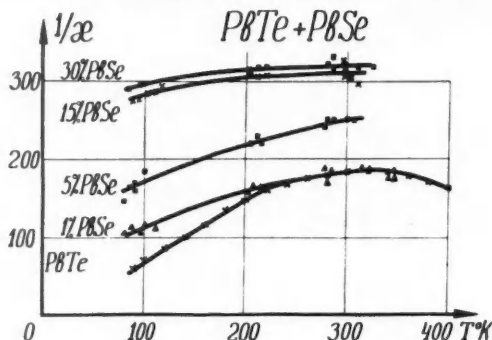


FIG. 5.

representing the heat resistivity of PbTe with addition of different amounts of PbSe (Fig. 5).

We devoted a good deal of work to the investigation of impurities. The guiding idea is simple enough: every foreign atom introduces an additional scattering center of a definite cross section.

Denoting by λ_0 the free path of phonons in a non-disturbed lattice and by a the lattice constant, we get for small concentrations N/N_0 :

$$(3) \quad \frac{\kappa_0}{\kappa} = 1 + \frac{N}{N_0} S \frac{\lambda_0}{a}$$

where $S = S_0/a^2$ stands for the cross section of an atom expressed in lattice units. The expression (3) takes into account both the quantity of impurities and the kind of distortion they produce. Experiments on various semiconductors revealed some cases of interstitial impurities with $S > 1$ up to $S = 10$. For instance an introduction of Te atoms in the lattice of GaSb leads to $S = 7$; in the same substance Se gave $S = 3$.

It seems that in some cases S must be taken as $S < 1$. For instance, a clustering in groups of n atoms leads to $S = n^{-1}$. For $n \cong 10$, $S = 0.46$. For most of

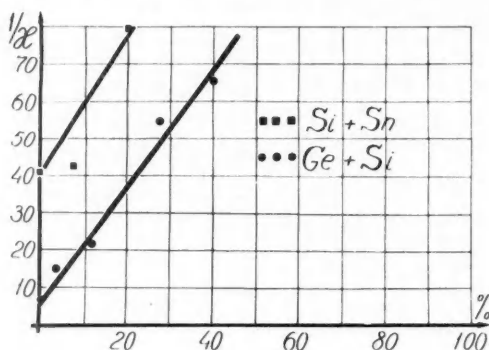


FIG. 6.

the semiconductors investigated so far the formula (3) holds good on the condition that $S = 1$ for substitutional impurities; for instance Si in Ge, Sn in Si, Se in PbTe (Figs. 6, 7). In accordance with (3) the influence of

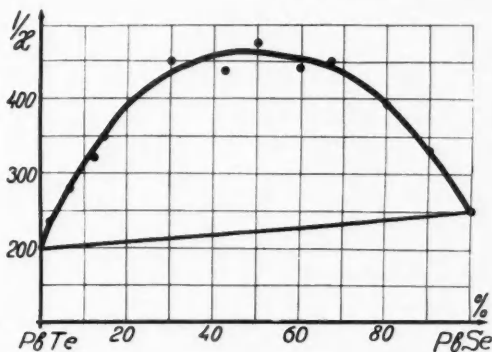


FIG. 7.

impurities is the more pronounced the larger is the free path λ_0/a . A contamination of Si (with $\lambda_0/a = 40$) or Ge (with $\lambda_0/a = 30$) is already noticeable at $N/N_0 = 10^{-2}$ (1% of impurities), while in PbTe (with $\lambda_0/a = 3$) only 10% of impurities produce an equal effect.

Of special interest are solid solutions with high impurity content. As soon as the concentration approaches 50% the lattice becomes irregular. Experiment shows in fact that the free path decreases in this case down to one to two atomic distances. Thus the heat conductivity approaches values which are typical of amorphous substances. For Ge κ decreases from 0.145 to 0.008, and correspondingly λ from $\lambda_0 \simeq 35a$ to $\lambda \simeq 2a$.

On the graph (7) the phonon heat resistivity $1/\kappa_{ph}$ is plotted against concentration of PbSe in PbTe. κ_{ph} is defined as $\kappa - L\sigma$. For a mixture of small crystals, the same diagram would be of the form of a straight line.

If at some concentration a new chemical substance appears the curve shows a steep peak.

For semiconductors with a large free path of phonons, $1/\kappa$ rises quickly with the introduction of impurities. For Ge with $\lambda_0/a \simeq 35$, 1% of impurities increases the thermal resistivity by 35%, while for PbTe with $\lambda_0/a \simeq 3$ the resistivity would increase by 3% only.

Thus thermal conductivity measurements may be developed to one of the most sensitive methods for the investigation of imperfections of a crystal lattice.

While the thermal conductivity of solid solutions becomes quite small, the mobility of electrons does not decrease at the same rate and even rises in some cases, for instance for the solutions of HgTe in HgSe.

It is obvious that such a behavior is highly profitable for thermoelectric couples. We ascribe the difference to a difference of wavelength. For non-degenerate electrons the wavelength is of the order of about 20 atomic

distances, while the wavelength of acoustical waves is considerably less. However, this question has to be considered more carefully.

The next most important question concerning semiconductors is the way phonons and electrons combine in the heat transport. Assuming they act independently, and this is reasonable up to a concentration of electrons of 10^{20} cm^{-3} , we may express the heat conductivity by the formula:

$$(4) \quad \kappa = \kappa_{ph} + L\sigma,$$

where

$$L = (r+2)(\kappa^2/e^2)T$$

for nondegenerate systems. Here r has the meaning of the exponent in the expression for the free path l as a function of energy

$$(5) \quad l \sim \epsilon^r.$$

As the free path cannot be measured directly, one might define r using the dependence of the mobility u on the temperature T :

$$(5a) \quad u \sim T^{(r-3/2)}.$$

For electrons in a degenerate state the factor $(r+2)$ has to be replaced by

$$(4a) \quad \frac{1}{3}\pi^2$$

independent of the mechanism of scattering of electrons. We were able to check the relations (4) and (4a) by introducing impurity atoms and in this way changing to a large degree the electrical conductivity σ without affecting the phonon conductivity κ markedly.

On Fig. 8 the heat conductivity κ is plotted against σ . Between $\sigma = 1000$ and $\sigma = 2500 \text{ ohm}^{-1} \text{ cm}^{-1}$ the electrons must be considered as nondegenerate,

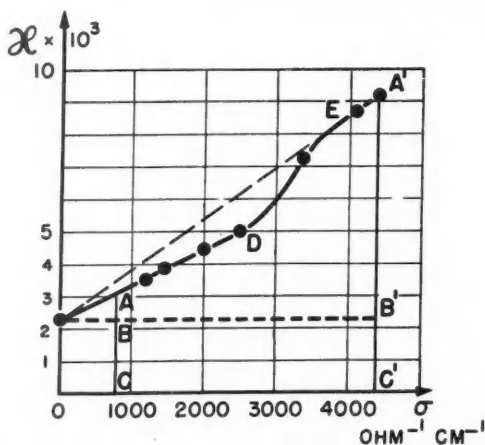


FIG. 8. Dependence of thermal conductivity on electrical conductivity. —, $\kappa = \kappa_{ph} + \kappa_e$; ---, κ_{ph} ; AB and $A'B'$, κ_e ; D , beginning of degeneracy; E , electron system degenerate.

while beyond $\sigma = 3500$ the concentration of free electrons exceeds 3×10^{19} and the electrons have to be considered as degenerate. Accordingly, we get $L = 2.2 \times 10^{-8}$ in the first case and $L = 3.3 \times 10^{-8}$ in the second.

For PbTe, where we have good ground to expect $r = 0$, as for the case mentioned above, Devyatкова has obtained 1.92 for the factor $(r+2)$ instead of 2 and in the degenerate state 3 instead of 3.3.

A deviation from the general rule has been first noticed in PbTe by Devyatкова in 1952 (Fig. 4). The resistivity increased linearly with temperature up to 200° K. only. Then the value of $1/(\kappa - L\sigma)$ deviated from a straight line more and more as the temperature rose. The behavior of PbTe at those temperatures suggested the idea of an additional mechanism of energy transport. Since that time we have been trying to find an explanation for such a mechanism. In 1940 Davydov and Shmushkevitch* considered the energy transport by a bipolar diffusion due to a recombination of electrons and holes, and gave for the additional heat conductivity $\Delta\kappa$ the following formula:

$$(6) \quad \Delta\kappa_{D.S.} = 2L \frac{\sigma_+ \sigma_-}{\sigma_+ + \sigma_-} \left[\frac{\Delta E_0}{2kT} + r + 2 \right]^2.$$

Price (1954) and Madelung (1956) suggested the same expression. However $\Delta\kappa$ computed on the basis of (6) is several orders of magnitude lower than the actual value.

In 1954 Busch noticed the analogous phenomenon on InSb.

Among the semiconductors investigated from this point of view we found some instances showing $\Delta\kappa$ surpassing $\Delta\kappa_{D.S.}$ many times: Ge, HgSe, HgTe, AgFeS₂ . . . (Fig. 9).

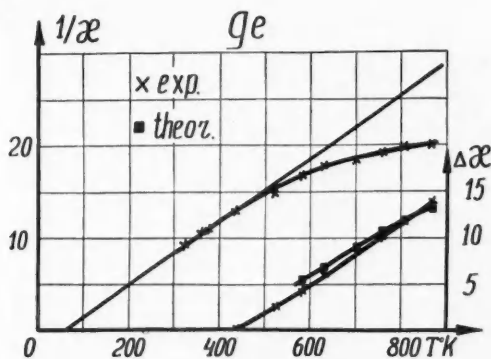


FIG. 9.

On the other hand no traces of $\Delta\kappa$ could be detected on Te in spite of a marked intrinsic conductivity.

There exist semiconductors with small ΔE_0 , such as Bi₂Te₃, Sb₂Te₃, Sb₂Te₃ + Bi₂Te₃, where the observed $\Delta\kappa_{D.S.}$ is in fair agreement with $\Delta\kappa_{D.S.}$. Goldsmith

*Uspekhi Fiz. Nauk, **24**, 21-67 (1940). (Advances of Physical Science.)

reported the same for monocrystals of Bi_2Te_3 (Fig. 10). Although the phenomenon expressed by the formula (6) cannot be denied, some other process besides the bipolar diffusion of electrons and holes may take place even before intrinsic conductivity becomes dominant.

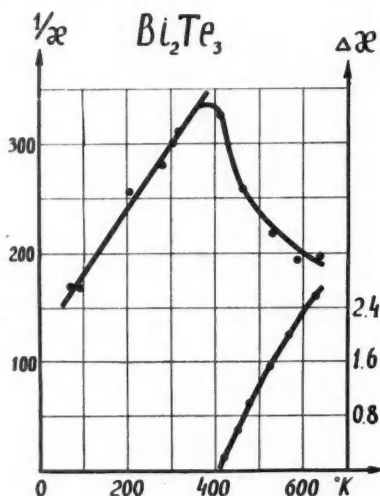


FIG. 10.

The situation is demonstrated on Fig. 11, representing PbTe . The electric conductivity σ , the Hall coefficient R , the thermoelectric power per degree α , and the heat resistance $1/(\kappa - L\sigma)$, have been measured in the range of temperatures from 90° K. to 750° K.

The curves of σ , R , and α show clearly that the intrinsic conductivity σ_{in} is undetectably small up to 450° K. Nevertheless a deviation of $1/(\kappa - L\sigma)$ from linearity starts already at 200° K. and exceeds many times the calculated $\Delta\kappa_{\text{D.S.}}$.

From Fig. 11 we may conclude that the carriers of the additional heat do not carry electric charges. The energy transmitted rises steeply with rise in temperature. By plotting $\log \Delta\kappa$ against $1/T$ we find that a practically straight line relation exists, thus showing that some excitation energy ΔE is required; we see at the same time that ΔE is considerably smaller than the width ΔE_0 of the forbidden zone.

There is ground enough to guess that the energy carriers may be identical with the excitons first introduced in 1931 by Frenkel. During the last few years E. Gross has investigated the absorption spectra of excitons of a number of semiconductors (Cu_2O , CdS , HgI_2 ...). Both the hydrogen-like structure of the spectrum and its behavior in a strong electric and magnetic field are consistent with the picture of a positronium inside a dielectric. Assuming that such unseparated pairs of electrons and holes may be produced by heat

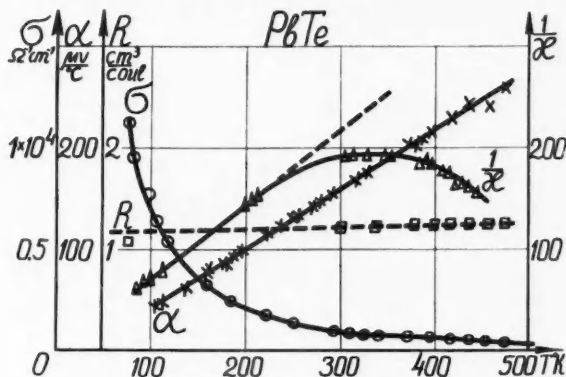


FIG. 11.

movement in a similar manner to free charges, we have thus a tentative explanation for additional heat transport.

In passing from hotter parts to colder ones the excitons give up their excitation energy and their kinetic energy to the lattice. Pickus developed an expression for the increase of heat conductivity due to excitons:

$$(7) \quad \Delta\kappa_{\text{ex}} = \frac{16}{3} \pi k \frac{(kT)^2}{h^3} m_{\text{ex}} l_{\text{ex}} \exp \left\{ -\frac{\Delta E_{\text{ex}}}{kT} \left[\left(\frac{\Delta E_{\text{ex}}}{kT} + 2 \right)^2 + 2 \right] \right\}$$

where m_{ex} is the effective mass, l_{ex} the mean free path, and ΔE_{ex} the excitation energy. The magnitude of $\Delta\kappa_{\text{ex}}$ cannot be computed so far, as m_{ex} , l_{ex} , ΔE_{ex} are not given by experiment. We may however proceed as follows: by plotting $\log \Delta\kappa$ against $1/T$ we find $(\Delta E_{\text{ex}})_{T=0}$ in a first approximation and correct the value of $(\Delta E_{\text{ex}})_{T=0}$ to fit the dependence of $\Delta\kappa$ on temperature, assuming $l_{\text{ex}} \sim 1/T$; it follows that $\Delta E_{\text{ex}} = 0.12$ ev. As for the effective mass m_{ex} , we put tentatively $m_{\text{ex}} = 2m_0$. The expression (7) leads then to $(l_{\text{ex}})_{T=300^\circ\text{K.}} \cong 10^{-6}$ cm., which is reasonable.

As concerns PbTe we have good ground to suppose that ΔE_{ex} increases with the temperature. We assume $\Delta E_{\text{ex}} = (\Delta E_{\text{ex}})_{T=0} + \alpha T$, where for α we use the same value as is known for the width of the forbidden zone—approximately $dE/dT = 4 \times 10^{-4}$ ev./deg. $(\Delta E_{\text{ex}})_{T=300}$ has then a value of 0.24 ev.

There are some indications in the absorption spectrum of PbTe of exciton levels of similar energy. The spectrum shows the first steep fall at 0.62 ev., corresponding to the forbidden zone; there follows a weak tail down to 0.25 ev. If we ascribe the tail to excitons we get an excellent check for the exciton hypothesis.

A thorough investigation of the absorption spectrum would be the best proof for the exciton hypothesis. One would expect for instance that at low temperature the long wave limit of the spectrum will shift to 0.12 ev. Beginning with 200° K. a gradually increasing absorption ought to appear at

$$\Delta E_0 - \Delta E_{\text{ex}} \cong 0.6 - 0.25 = 0.35 \text{ ev.}$$

corresponding to a transition of an electron from the exciton level to the free band.

We are now in search of such a proof. The case of PbTe is encouraging. But there are no indications of an infrared tail in Ge, while the same reasoning would lead to

$$(\Delta E_{\text{ex}})_{T=0} = 0.21 \text{ ev. for Ge.}$$

In the case of Te we have to assume that the excitation energy of excitons is nearly equal to the width of the forbidden band.

Besides the exciton hypothesis some more explanations have to be taken into consideration. A drag of phonons by the bipolar diffusion of pairs or of excitons will transport energy. A diffusion of plasma waves will have the same effect. At high temperatures energy will be transmitted by electromagnetic radiation. Genzel has computed the corresponding $\Delta\kappa$:

$$(8) \quad \Delta\kappa_{\text{rad}} = \frac{16}{3} \frac{a\epsilon}{k} T^3$$

where ϵ is the electronic part of the dielectric constant and a is the factor in Stefan's law.

A peculiar kind of additional energy transport has been considered by Ayrapetyanz in our laboratory.

If we have some amount of a substance with a thermoelectric power α_i , while the enclosing medium has $\alpha = \alpha_0$, closed thermoelectric currents develop Peltier heat, increasing the heat conductivity by an amount:

$$(9) \quad \frac{\Delta\kappa_\alpha}{\kappa} = \frac{2}{3} \sum_i c_i \frac{(\alpha_i - \alpha_0)^2}{\kappa_0} \sigma T$$

where c_i is the concentration of the phase i . For $c_i = 0.5$, $\alpha_i - \alpha_0 = 300 \mu\text{v./degree}$, $\sigma = 1000 \text{ ohm}^{-1} \text{ cm.}^{-1}$, $\kappa = 0.02 \text{ watt/cm. deg.}$, we would have $(\Delta\kappa/\kappa) \cong 0.5$. A prolonged tempering decreases $\Delta\kappa_\alpha$ considerably. For metals and for semiconductors with small σ , $(\Delta\kappa_\alpha/\kappa)$ is less than 0.1%.

All phenomena considered so far lead to an increase of thermal conductivity. If however the concentration of free charges exceeds 10^{20} cm.^{-3} the scattering of phonons by electrons markedly decreases κ_{ph} .

Summing up the evidence obtained in the course of our investigation, we see that the problem of heat conduction by both phonons and electrons is quite involved. The hypothesis of simple additivity expressed by the formula (1) and (4) is restricted to the case of charge carriers of one sign only. Even then one has to choose the right value of L , depending on the manner of scattering. In fact L may change between $L = (k^2/e^2)T$ and $L = 4(k^2/e^2)T$. For metals on the other hand L has the same value $L = \frac{1}{3}\pi^2(k^2/e^2)T$, but the first term $-\kappa_{\text{ph}}$ —nearly disappears.

As soon as a bipolar diffusion of free charges or of unseparated pairs (excitons) becomes appreciable a new kind of heat transport is added, increasing the thermal conductivity many times.

A large variety of other physical phenomena may be involved in heat transport in semiconductors. They all may take place simultaneously. It has

to be determined which of them is the essential one under given circumstances.

We consider our work as the beginning of an investigation of thermal properties of semiconductors.

The experiments discussed in this paper were performed by Mrs. A. Joffé, Mrs. E. Devyatkova, and by P. Gulyaev.

DISCUSSION OF JOFFÉ'S PAPER

Mott: Could Professor Joffé tell us whether all insulating substances have an exciton band appearing in their optical spectra?

Joffé: There is no sign of an exciton band in tellurium and germanium. Perhaps there may be one, but too close to the conduction band to be observed.

Mott: You would expect only a small gap in a substance of high dielectric constant.

Joffé: Gross believes that only substances with a high photoelectric effect have an exciton band. This is in a way quite amusing, as it is exactly the opposite of what Frenkel said when he conceived the idea of excitons: namely, that the excitons would provide non-conducting excited states and hence account for the absence of photoconductivity. Our experiments prove that excitons may be produced by heat movement and are free to move.

Mott: According to Apker, an exciton will wander about the solid until it reaches an impurity, where the electron is released as a charge carrier.

Aigrain: There is an alternative explanation for the absorption spectrum of PbTe described by Professor Joffé. This is to say that the main absorption band is due to direct transition, while the tail is due to indirect transitions involving phonons. This is observed in PbS.

Joffé: I believe that the photoelectric effect in semiconductors is generally associated with a primary formation of excitons. But I should be interested to discuss this matter with you later.

Ziman: In a paper by Berman, Foster, and Ziman, shortly to be published, it is shown that in many substances (e.g., Ge and Si) the thermal conductivity at low temperatures is dominated by the scattering of phonons by the natural distribution of isotopes. These act as impurity centers and give Rayleigh type scattering, so that the conductivity tends to proportionality to T^{-1} instead of showing the exponential rise at low temperatures typical of the influence of Umklapp processes.

Price: Let us consider InSb. When I calculated the exciton contribution, the formula turned out to be the same as that of Pickus quoted by Dr. Joffé, except that firstly I used values of the mean free path calculated from the theory of Anselm and Firsov, and secondly I included a factor for the "many valley" degeneracy, and also the spin degeneracy, of the bands. This factor is not small. The final result was a contribution to thermal conductivity only of the same order as the ambipolar contribution. Thus it does not account for the experimental results of Busch and Schneider. It must be remembered, however, that, because of the large Bohr radius (about 700 Å) of an exciton according to the "positronium" model, at the temperatures where Busch and

Schneider observed their effect the calculated exciton density is many times the inverse of the exciton volume. This means of course that the calculation is invalid. There remain the following two possibilities to explain the observations: First, the exciton state may be of "deep trap" character. Then the difficulty disappears and the calculation is valid because the exciton volume is of the order of a cell volume. Also one then calculates a higher exciton density and can in fact hence obtain predicted thermal conductivities as large as the observed ones. This deep trap is hard to believe for InSb because of the small electron mass—but the results on excitons which Dr. Joffé reported encourage the hypothesis. It may well be that the electron-hole interaction is stronger than the Coulomb interaction. This should be investigated. The second possible explanation is that energy is transported by a plasma mode in which electron and hole concentrations fluctuate in phase.

Now let us consider what experiments are suggested by the present situation:

(1) In silicon the gap in the valence band from the p bands with $j = 3/2$ to the p band with $j = 1/2$ is thought to be only 0.035 ev. Consequently there might be an ambipolar effect in p -type Si above 300–400° K. involving only these two hole bands.

(2) In a crystal conducting heat by the ambipolar mechanism it may be possible to observe recombination radiation at the cold end. For example in germanium at room temperature there is a flux of 10^{14} pairs per cm^2 sec. for a gradient of one degree per cm. Of course it depends on the quantum efficiency at the cold surface. The same possibility exists for excitons, and hence perhaps by the recombination spectrum one could distinguish between the mechanisms in the various substances.

(3) There is the possibility of a thermoelectric anomaly from an exciton drag effect, in which the excitons are entrained by the charged carriers when there is an electric current. The order of magnitude of the contribution to the Peltier coefficient is

$$\left(\frac{\text{mass of charged carrier}}{\text{mass of exciton}} \right)^{\frac{1}{2}} \times \left(\frac{\text{m.f.p. of exciton}}{\text{m.f.p. of charged carriers for collisions with excitons}} \right) \times \left(\frac{\text{potential of creation of exciton}}{\text{exciton}} \right).$$

It looks as though the effect is small, but perhaps it is appreciable for p -type InSb.

A further contribution to the discussion was made by **Aigrain**, who described similar work on semiconductors carried out in Paris. Where the phonon mean free path was less than the electron wavelength, the phonon lost its individuality as regards its interaction with electrons: this lessened the electron mobility. On the other hand the mobility of an *exciton* could be

fairly large; for example, in CdSe the diffusion constant for excitons was ten times larger than that for electrons. **Price** replied that the mean free path of excitons might tend to be longer than for electrons or holes because the deformation potential appropriate to excitons was the change of forbidden gap with strain, and in general the band-edge energies should move the same way under strain and hence their changes would tend to cancel each other in the change of gap.

ON THE TRANSITION TO METALLIC CONDUCTION IN SEMICONDUCTORS¹

By N. F. MOTT²

ABSTRACT

A discussion is given of the conductivity to be expected from a crystalline array of atoms when the interatomic distance a is varied. It is shown that both for monovalent atoms and divalent atoms the conductivity is zero at $T = 0$ when a is large, the wave function of the system being real so that no current is possible. In both types of atom a discontinuous transition to a state showing metallic conductivity is predicted at a definite value of a . For divalent atoms calculations using Bloch orbitals and localized Wannier functions give essentially the same result; for monovalent metals they do not, and correspond to physically different states of the system. Applications are made to impurity-band conduction in semiconductors, the impurity centers being treated by the usual model as expanded atoms in a uniform dielectric. It is shown that the concentrations at which "metallic" conductivity sets in are not unexpected, but that it is difficult to understand impurity band conduction at lower concentrations unless the semiconductors are "compensated", either chemically or through the presence of dislocations.

1. INTRODUCTION

In two papers (Mott 1949, 1952) the present author has discussed the difference between metals and non-metals and the behavior of materials such as the oxides of nickel and cobalt, which are insulators when pure but which ought to be metallic conductors according to a crude application of the Bloch-Wilson theory of metals. The aim of this paper is to give a more detailed treatment of this problem, and to apply it to the behavior of a semiconductor containing a high concentration of impurity centers.

The question examined in the author's previous papers and here is that of the electrical conductivity of a cubic lattice of similar atoms. As a mathematical problem it may be supposed that the lattice parameter a or distance between the atoms can be varied continuously. The atoms in their ground states may have either a spin (for example a monovalent atom such as hydrogen or sodium) or no spin (divalent or rare gas atoms). The thesis presented in this paper is that in both cases the electrical conductivity at the absolute zero of temperature will be zero when the lattice parameter a is large. If a is decreased, then at a certain value a_0 there will be a *sudden* transition to a state described by electronic wave functions having a different form in which the electronic conductivity is of the same order as that to which we are accustomed for metals. This prediction is quite different from that of the Bloch-Wilson theory, according to which a lattice of monovalent atoms will always conduct although the effective mass will be large for large values of a , while for divalent atoms the number of free electrons will at first be zero and will remain zero until overlap into the second zone begins, and will then increase steadily with no discontinuous change.

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²Cavendish Laboratory, Cambridge, England.

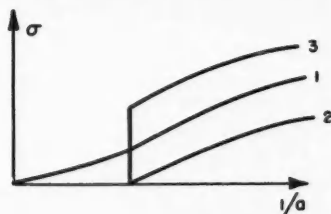


FIG. 1. Conductivity (or number of free electrons divided by effective mass) as a function of the interatomic distance.

1. Monovalent metal according to Bloch's model.
2. Divalent metal according to Bloch's model.
3. Any metal according to the theory of this paper.

The application of the theory considered in this paper is to the conductivity of semiconductors containing a high concentration of donor or acceptor impurities and to the conduction by electrons in the impurity bands of semiconductors.

2. THE ELECTRICAL PROPERTIES OF AN ARRAY OF MONOVALENT ATOMS

In this section we shall discuss first the properties of a three-dimensional array of atoms each containing a single electron. The lattice may or may not contain in addition other atoms with closed shells, such as oxide ions. The discussion with small changes would be applicable to cupric ions and thus to CuO , to doubly charged nickel ions but not to divalent metals.

First of all we suppose the atoms to be far apart and each atom to have an electron affinity* E and ionization potential I . If there is only small overlap between the atomic orbitals, the Bloch model suggests that there should be a half-filled band and that the material should show metallic conductivity though with a high effective mass. Common sense would, however, suggest that the material will be an intrinsic semiconductor with activation energy $I-E$, and thus have a conductivity which tends to zero as the temperature tends to zero. If, however, the wave functions of two adjacent atoms overlap at all, one knows that the exact wave function will include terms which allow for the finite probability of the presence of polar states, in which one atom contains two electrons and an adjacent atom none. This property of wave functions is sometimes believed (cf. Heikes 1955) to lead to conductivity, in crystals for which it occurs. We consider that this is incorrect, because normally the form of the wave function ensures that the regions in space where the extra electron is present and where the electron is absent remain close to each other, so that there are no free carriers. This we shall now attempt to prove.

For an electron moving in a periodic field due to N atoms, there are N Bloch wave functions $\psi_k(\mathbf{r})$ possible in the first band for each spin direction. The usual description of the wave function of a monovalent metal is a determinant or sum or determinants using *half* these wave functions, the half with the

*By the electron affinity we mean the energy released when a singly-charged negative ion is formed.

lowest energy. These wave functions describe a state which can carry a current because the excited states of the system lie very close to the ground state, being separated from it by an energy which tends to zero as N tends to infinity. It is thus possible, for energies of the whole system very near to that of the ground state, to set up *complex* wave functions, which according to wave mechanics can describe a state with a current.

It is, however, possible from the N wave functions in the first band to set up a set of orthogonal wave functions, the Wannier (1937) or Löwdin (1950) functions $w_n(\mathbf{r})$, which are *localized*, one round each atomic site; here the suffix n denotes the site. If the material is antiferromagnetic we may set up for each site a wave function

$$w_n(\mathbf{r})\chi_\alpha(\sigma) \quad \text{or} \quad w_n(\mathbf{r})\chi_\beta(\sigma),$$

the functions χ_α, χ_β being spin wave functions for the two spin directions, and from these we may form a *single* determinant (not a sum) to describe the state of the whole system. The properties of this wave function are:

- (a) It is real, and therefore does not describe a state carrying a current.
- (b) The only state with the same or nearly the same energy is that in which *all* the spin directions are interchanged, except states formed by the excitation of spin waves, which are known not to carry a current.
- (c) If it is treated as an approximation to an exact wave function, we see that the first excited state with zero spin will be formed by substituting for one of the $w_n(\mathbf{r})$ an *excited* atomic wave function, which will take an energy of order I (several electron volts).

(d) Since the wave functions $w_n(\mathbf{r})$ overlap, polar states are present, in the sense that the wave function allows the presence of two electrons on one atom; but since the wave function is real this cannot lead to a current. The polar states therefore do *not* lead to mobile charge carriers so long as the state of the crystal is correctly described by this kind of wave function. This is because the holes and electrons in the lowest state wave function are bound to each other in space.

For crystals containing *two* electrons per atom, it is well known that the determinant formed from Bloch wave functions and that formed from localized (e.g. Wannier) functions are identical, both describing a non-conducting state; but for crystals with *one* electron per atom they are not the same. The above considerations show that the two wave functions then correspond to different states of the crystal, one conducting (and with an electronic specific heat linear in T and with other metallic properties), and the other non-conducting. They are thus not alternative zero-order descriptions of the exact function; they correspond to different states of the system, the true one at the absolute zero in each case being that with the lower energy. The wave function formed from Wannier functions will clearly give the lowest energy for large interatomic distances; the existence of metals leads us to believe that the other gives the lower energy for small ones. We shall give below arguments in support of the

hypothesis that the transition is sharp, and some estimate of the interatomic distance for which the transition occurs.

We have assumed up to this point that the non-conducting wave function describes an antiferromagnetic arrangement of spins. There are other possibilities—that it may be ferromagnetic or paramagnetic without any long-range order in the directions of the spins. We do not know of any non-conducting material corresponding to the second case, nor whether such a case can exist. For ferromagnetic non-conducting materials the argument would be the same as that given above; one can set up a single determinant as a first approximation to the wave function, so that the wave function is real and cannot describe a state in which a current flows.

In either the ferromagnetic or antiferromagnetic case, by reversing the spin of one or more electrons and setting up the wave functions corresponding to a spin wave one can obtain excited states with excitation energies tending to zero as N tends to infinity. One can therefore set up complex wave functions. But it is known that a spin wave cannot carry a current, the current vector corresponding to a wave function describing a spin wave being zero. This theoretical prediction corresponds to the observed fact that antiferromagnetic materials show an exponential increase in conductivity (as $e^{-W/kT}$) as the temperature is raised, while the number of spin waves excited is believed to be proportional to $T^{3/2}$.

3. SLATER'S MODEL FOR SUBSTANCES OF THE NICKEL-OXIDE TYPE

Slater (1951) has suggested that antiferromagnetic substances of the nickel oxide type should be described by Bloch wave functions and their non-conducting properties described as follows. Any electron described by a Bloch wave function will, in terms of the Hartree-Fock equation, be repelled considerably less by electrons with spin in the parallel direction than by electrons with spins in the antiparallel direction. Therefore in a crystal in the antiferromagnetic state each electron will move in a crystalline field on which is superimposed that of a superlattice. This field of a superlattice will split the first zone of a cubic lattice into two, each containing $\frac{1}{2}N$ states for each spin direction. With one electron per atom, the first zone could be completely full and the second empty. The material would then be an insulator.

While this model certainly gives a possible first approximation for an antiferromagnetic substance, it is misleading in one respect. It suggests incorrectly that the material will show metallic conductivity above the Néel point, or in other words that the activation energies required to destroy the long-range antiferromagnetic order and to produce current carriers are of the same order of magnitude, both depending on the width of the energy gap. In fact the former will depend on some overlap integral giving the strength of the exchange or super-exchange interaction, which will tend to zero as a tends to infinity. The activation energy for conduction, on the other hand, tends to $I-E$. On the other hand Slater's model is probably the most convenient for the description of metallic materials such as chromium that are antiferromagnetic (Lidiard 1953, 1954).

4. THE SHARPNESS OF THE TRANSITION FROM THE NON-METALLIC TO THE METALLIC STATE

We have stated above that we expect as a is decreased a *sharp* transition from the non-conducting state to the metallic state with a finite number of free electrons. This we believe will occur either for monovalent or for divalent atoms. Our reasons are as follows. Let us start, in the case of a lattice of monovalent atoms, with a wave function which is a single determinant of Wannier functions describing an antiferromagnetic arrangement of spins. If an *extra* electron is added to such a material, it can of course move freely through it as through any other insulator, and the energies of such an electron will form a "conduction band". Similarly if an electron is removed a mobile positive hole is formed. We may ask what is the minimum energy W necessary to form a free electron and a positive hole. When the atoms are far apart we have

$$W = I - E.$$

As they come closer W will decrease. But W cannot tend to zero. The reason is that an electron and a positive hole attract each other with a force of which the potential energy for large r is $-e^2/\kappa r$, where κ is the dielectric constant. It is known that, whatever happens for small r , bound states always exist for pairs of particles which attract each other with a force which tends at large distances to the Coulomb form, the binding energy being of order $me^2/2\hbar^2\kappa^2$. Thus a *small* number of free carriers is impossible in the ground state, whether for mono- or di-valent substances, because the free carriers of positive and negative sign will combine to form pairs (similar to positronium atoms). The argument does not of course apply when there is a *large* number of free carriers; here, according to the work of Bohm and Pines, any pair of charged particles may be thought to attract each other with a force derived from a screened potential $(-e^2/\kappa r)\exp(-qr)$, the screening being due to the other electrons. Such a potential does not necessarily lead to a bound state.

We consider therefore that the plot of W against $1/a$ should be as sketched in Fig. 2.

It is of interest to make an estimate of the value of $1/a$ for which the transition from a conducting to a non-conducting state occurs. Without attempting an exact calculation, we can say at once that the overlap between adjacent

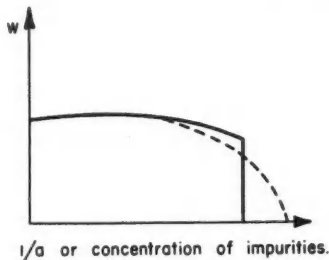


FIG. 2. Activation energy of an extrinsic semiconductor as a function of the distance a between impurity centers. Full line: theory. Dotted line: observed.

atoms must be large, so that the overlap and exchange integrals are a significant fraction of $I-E$. We assume that the metallic state is non-ferromagnetic; otherwise it would not conduct if we have one electron per atom in an s state. Then the use of Bloch wave functions will mean that the fraction of its time that an electron spends in atoms where there is another electron with anti-parallel spin will be quite large, say 50%, depending on the importance of the term in the wave function describing correlation. Thus the energy of the Bloch wave functions must be lowered by a term of order $\frac{1}{2}(I-E)$ before the metallic state can have the lower energy. This will certainly involve large overlap between atomic (or Wannier) orbitals.

A more quantitative estimate can be made using Slater's model of the value of $1/a$ at which a transition occurs from the antiferromagnetic non-conducting state to a hypothetical conducting but still antiferromagnetic state. For this purpose let us consider a body-centered cubic lattice and denote the side of the unit cell by b . The atoms on one simple cubic lattice will all have the same spin direction; we shall describe them by Bloch wave functions

$$\psi = \sum \exp(ikr_l) \phi(r-r_l)$$

with energies

$$W = -2\gamma(\cos k_x b + \cos k_y b + \cos k_z b),$$

where (k_x, k_y, k_z) is the wave vector, γ an overlap integral, and ϕ an atomic hydrogen-like wave function. This band is full for electrons of the spin considered; we have to ask whether the top of the band, with energy 6γ , overlaps the bottom of the band obtained when an *extra* electron from the lower band is brought into the other half lattice occupied by electrons of opposite spin. If the depth of the bottom of this band is $-w$, the condition for conductivity is

$$6\gamma + w \geq I - E,$$

where I is the ionization energy for one of the atoms, and E the electron affinity. We might equate w to $6\gamma'$, where γ' is an overlap integral for the extra electron moving from one otherwise neutral atom to another; this overlap will, however, be large and we prefer to set for the wave function of the extra electron a plane wave, so that $-w$ is the averaged potential energy of the electron.

Thus

$$\begin{aligned} \gamma &= \int \phi^*(r) \phi(r-r_1) (e^{-2/r}) d\tau \\ &= (me^4/2\hbar^2)(1+b/a_H) \exp(-b/a_H), \end{aligned}$$

(Bethe 1933), where a_H is the hydrogen radius; also

$$w = \int V(r) d\tau / \int d\tau$$

where $V(r)$ is the potential within a hydrogen atom so that

$$V(r) = e^2 \left(\frac{1}{a_H} + \frac{1}{r} \right) \exp \left(\frac{-2r}{a_H} \right)$$

and the integration is over a sphere of volume $\frac{4}{3}\pi b^3$. Neglecting small terms containing the exponential this gives

$$w \simeq 4\pi e^2 a_H^2 / b^3.$$

If we take $E \sim 0.1I$, as for hydrogen, this gives as the condition for conductivity

$$\frac{4\pi e^2 a_H^2}{b^3} + \frac{bme^4}{2\hbar^2} \left(1 + \frac{b}{a_H}\right) \exp\left(-\frac{b}{a_H}\right) \geq 0.9 \frac{me^4}{2\hbar^2}.$$

A numerical solution gives

$$b/a_H \simeq 4.5.$$

A convenient way of expressing this is to introduce the ratio X of the radius of the atomic sphere round each atom to a_H , so that the number c of atoms per unit volume is

$$c = 2/b^3 = 3/4\pi X^3 a_H^3.$$

The critical value of X at which the transition to the metallic state should occur is then given by

$$X \simeq 2.2.$$

These considerations do not take into account the fact that the first few electrons which overlap should form "excitons" with positive holes. The value given above may thus be a slight underestimate. We have not as yet attempted any calculations of the energies of formation of these excitons, or the concentration at which they should dissociate.

5. THE CASE OF DIVALENT ATOMS

The position is here somewhat different. Let us suppose as before that the atoms are arranged in a cubic lattice. Then, starting from the Bloch approximation, there are enough electrons just to fill the first Brillouin zone. If in k -space there is no overlap into the next zone, we can say:

(a) The state described is non-conducting.

(b) The determinantal wave function describing the state of the whole system is the same, whether we use Bloch or Wannier functions.

Therefore the transition from a non-conducting to a conducting state does not involve any sudden change in the form of the wave functions, as is the case for atoms with one electron. We can thus envisage a state in which the overlap into the second zone is very small, so that, if there are n electrons and n holes per atom, n is small compared with unity. But if n is very small, we would expect the electrons and holes to form pairs (like positronium atoms), so that the state will be non-conducting. A conducting state can only arise when there are enough "positronium" atoms to interfere with each other, so that they break up. We do not know how to make a numerical estimate of this, but suggest that it will occur when

$$n \sim 1/r_0^3$$

where r_0 is the radius of the "positronium" atom, so that

$$r_0 \sim \hbar^2/m_{\text{eff}}e^2.$$

Thus the transition will be of the same general type as that illustrated in Fig. 2.

It is noteworthy that the only metals with a very small number (*ca.* 10^{-5}) of carriers per atom are bismuth and similar metals in which m_{eff} is abnormally small. For bismuth m_{eff} is a tensor; its magnitude is as small as $10^{-2} m$ in one direction (Heine 1956), so a value of n as small as observed is consistent with our theory.

6. APPLICATION TO SEMICONDUCTORS SHOWING CONDUCTION IN THE IMPURITY BAND

The interest of this phenomenon to the metal physicist is that the study on hydrogen-like impurity centers in silicon and germanium and similar materials provides perhaps the only way of investigating the electrical properties of an array of atoms as the interatomic distance is varied. Unfortunately, the centers are in a disordered, not a crystalline array, which complicates the issue. In this paper we shall treat the centers as hydrogen atoms in which the effective mass is m^* and the force attracting the electrons to the center $e^2/\kappa r^2$; complications due to anisotropy and degeneracy of the band are neglected.

A number of papers discuss impurity band conduction; recent ones with references to earlier papers are Carlson (1955), Fritsche and Lark-Horowitz (1954), and Aigrain (1954). In terms of the present theory we ought to distinguish between two quite different types of conduction which might be described as associated with impurities, but without thermal excitation into the conduction band.

The first type, mentioned by Aigrain (1954) but not always clearly distinguished from the second type by some early writers, can only occur in *compensated* semiconductors. Suppose that for instance an *n*-type conductor contains per unit volume c_1 donor levels and a smaller number c_2 of acceptor levels. Then all these acceptor levels will, at the absolute zero of temperature, be occupied and negatively charged. Of the donor levels $c_1 - c_2$ will be empty, and these vacant places (positive holes) can always move from center to center however small c_1 , provided there is some overlap between the wave functions of the electrons on adjacent donor centers. As c_1 decreases, the effective mass for this kind of impurity-band conduction increases.

As regards the activation energy for this type of impurity band conduction, we may distinguish two extreme cases. Suppose c_2 is small compared with c_1 . Then the current will be carried by a small number of holes in the assembly of occupied *n*-type centers. At the absolute zero, however, each of these holes will be bound to the nearest (negatively charged) acceptor. The binding energy W will be of order

$$W = e^2/\kappa(\frac{1}{2}r_0),$$

where r_0 is the average distance between donors ($c = r_0^{-3}$) and κ the dielectric constant. Both conductivity and Hall constant should thus vary with temperature as

$$\exp(-\frac{1}{2}W/kT).$$

The other more interesting case is when the compensation is nearly perfect, so that

$$c_1 \gg (c_1 - c_2).$$

We then have a small number $(c_1 - c_2)$ of electrons moving in the donor impurity band. This band is what has been termed "wavy"; this means that the potential energy at any one donor site depends on the surrounding immobile positive and negative charges which reside on the empty donors and full acceptors. Since these are distributed at random, we expect in space a random variation of potential. At the absolute zero of potential, the few mobile electrons will seek out the sites of lowest energy, so it would still seem that an activation energy is necessary for conduction. Certainly this will be so if c_1 is small so that the overlap between donors is small. However if the overlap is considerable it is possible that the sites which have lowest energy are not deep enough traps to have *bound* wave functions associated with them. We have to do here not with trapping centers around which there is a Coulomb field, but with centers of diameter about r_0 and depth a fraction of $e^2/\kappa r_0$. A rough calculation shows that bound states will disappear when r_0 is a multiple of $\kappa\hbar^2/me^2$, which means that overlap must be substantial. If there are no bound states, or only so few as to leave some unbound electrons in the impurity band, we expect a Hall constant which tends to a finite value as T tends to zero. As pointed out by Lehman and James (1955) too, the presence of mobile electrons as the temperature is raised will exert a screening effect, and tend to reduce the difference in energy between the various sites.

For large separation cited at low temperatures, however, it is difficult to resist the conclusion that the *mobility* should show an activation energy; although the barriers between the impurity centers will be passable by tunnel effect, the electron will settle down at sites of low energy and continual normal activation should be necessary to keep it in motion.

Turning now to the behavior of uncompensated conductors, we note that some writers on impurity band conduction have assumed implicitly, *with only one type of center*, that an array of singly charged centers can be treated as a half-filled band, the gap between this band and the conduction band decreasing to zero as the concentration increases. For the reasons given above, we consider this concept false. A *regular* array of monovalent dissolved atoms ought to behave like a metallic conductor only if the overlap is large, the transition to the metallic state will be sudden as the concentration increases, and in the metallic state the effective mass will not be abnormally large. We therefore expect a variation of activation energy with concentration such as that shown in Fig. 2. The observations of Pearson and Bardeen (1949) for *p*- and *n*-type silicon and of Debye and Conwell (1954) for *n*-type germanium seem to show a continuous transition of W to zero as shown by the dotted line in Fig. 2. It is of course possible that the random arrangement of atoms obscures the sudden change that one would expect for a crystalline lattice. If so the large drop in W before the metallic state is reached, which various calculations have failed to explain (e.g. Castellan and Seitz 1951), may be due to smearing out

of the discontinuous drop (Fig. 2). It seems to us unlikely, however, that the random arrangement of the atoms smears out the sharp transition from the metallic to the non-metallic states; according to our hypothesis the wave functions of the two states are quite different in form, and one has to ask, for either an ordered or a disordered state, which has the lower energy. If this is so, the observed gradual transition may well be due to an insufficiency of experimental points, and further measurements at smaller intervals of the concentration could be of great interest. It would also be of interest to observe the infrared absorption of the impurity centers as the concentration increases (compare Lax and Burstein 1955), under conditions of negligible compensation.

Comparing these theoretical findings with experiment, we show in Table I the values of the concentration c at which the activation energy tends to zero,

TABLE I

VALUES OF X , THE RATIO OF THE RADIUS OF THE ATOMIC SPHERE ROUND EACH IMPURITY ATOM TO THE RADIUS OF THE WAVE FUNCTION, FOR THE CONCENTRATION WHERE THE ACTIVATION ENERGY DISAPPEARS

	Germanium		Silicon		In Sb	
	Electrons	Holes	Electrons	Holes	Electrons	Holes
(1) Dielectric constant	16	16	12	12	14	14
(2) Mass (parallel)	1.4-1.58		0.8-1.0			
(3) Mass (perp.)	0.083		0.2			
(4) Mass (av.)	0.24	0.36	0.45	0.58	0.02	0.18
(5) Binding energy (calc.), ev.	0.009	0.019	0.030	0.055		
(6) Binding energy (obs.), ev.	0.013	0.011	0.044	0.057		
(7) Impurity for (6)	As	Ga	P	Al		
(8) $a_H \times 10^7$ cm.	3.5	2.3	1.5	1.1	3.6	3.7
(9) Critical value of $c \times 10^{-17}$ (obs.)	1.5-3	1.8	ca. 100	ca. 100	Small	ca. 10
(10) Reference* for (9)	(a), (b)	(b), (c)	(d)	(d), (c)		
(11) Value of X corresponding to (9)	2-4	4.8	1.9	2.6		2.5

Note:—The average effective masses shown in row (4) are those used by Kittel and Mitchell (1954) to calculate the binding energies shown in (5). They are then used to calculate the radius $a_H = \hbar^2 \kappa / m_{eff} e^2$ shown in (8). The critical values of c for which conductivity disappears have been estimated from the experimental data in row (9). The value X shown in (10) is the ratio $X = r/a_H$ where $c = 3/4\pi r^3$.

*References: (a) Debye and Conwell 1954; (b) Hung and Gliessmann 1954; (c) Fritsche 1955; (d) Morin and Maita 1954.

and attempt to deduce from them the quantity X (ratio of the radius r of the atomic sphere such that $c = 3/4\pi r^3$ to the radius of the orbit of the wave function of impurity center, assumed hydrogen-like). The values of this quantity X are found to range about our theoretical value 2.2, calculated admittedly for an ordered array assumed antiferromagnetic. We note that in addition the non-isotropic form of the effective mass makes this approximation very rough; also that these critical concentrations ought to be measured at very low temperatures, because (Lehman and James 1955) the activation energy at higher concentrations is greatly affected by the free carriers.

Both the papers of Baltensperger (1953) and Stern and Talley (1955) deal with concentrations on our model greater than this critical concentration.

Our analysis then suggests that for lower concentrations than these conduction should only occur if the semiconductor is compensated, and we are unable to propose an explanation of the finding of Fritsche (1955) and others that it occurs for concentrations a hundred times lower in the absence of any chemical compensation. It may however be tentatively suggested that dislocations play a role. If (Read 1955) a dislocation acts as an acceptor, then there will be round a dislocation line in a semiconductor of n -type a cylinder denuded of electrons and of radius $(c\pi d)^{-1/2}$, where d is the distance between charges on the dislocation. If d is a small multiple of an interatomic distance, say 10^{-7} cm., and $c \sim 10^{15}$ cm. $^{-3}$, this radius is 0.5μ . Along the circumference is a region where empty impurity levels are adjacent to full ones. Conduction in this region should involve a very small activation energy and lead to a Hall coefficient of the same order as that at high temperatures.

Note added in proof (October 16, 1956): Since writing this paper, it has been pointed out to the author by Dr. C. Herring that, when the separation between one-electron centers is large, the Heisenberg exchange integral is an order of magnitude smaller than the "hopping" integral which determines the frequency with which a carrier jumps from one center to another. Therefore at the concentration of impurity centers at which a transition to metallic conductivity occurs we cannot expect any antiferromagnetic correlation between the directions of the spins, as in the Slater model. Nevertheless the estimate given of the concentration at which a transition to metallic conductivity occurs should not be greatly in error; one still has to ask at what concentration will energy be gained by transferring a few electrons from neutral centers to others to form negatively charged centers.

Only since writing this paper, also, the author has read the review of the subject by E. M. Conwell (Phys. Rev. **103**, 51 (1956)) and has had the opportunity of discussing recent experimental work in the Bell and Watson Laboratories, New York. Conwell emphasizes the importance of "compensation", i.e. the presence of a certain number of acceptors in an n -type conductor. We emphasize our view that impurity-band conduction, below the critical concentration for metallic conduction, will *only* occur, for instance in an n -type conductor, if acceptors are present; that the carriers are "holes" (empty donors), and that the activation energy to free one from the nearest charged acceptor (at a distance r_0) is $e^2/\kappa r_0$. As regards the mobility, we know of no theoretical treatment. If for very low concentration the Hall effect disappears (as for conductivity in lithium-activated NiO), we must assume that the concept of a mean free path disappears and that the electron jumps from center to center.

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DISCUSSION OF MOTT'S PAPER

Frederikse: I have a possible explanation for the continuance of conductivity down to very low temperatures. In measurements of the Hall effect and thermal conductivity in Mg_2Sn (Frederikse, Hosler, and Roberts, 1956, *Phys. Rev.* **103**, 67) we have found that while different specimens may differ widely at high temperatures, at helium temperatures the Hall effect and the electrical conductivity are almost the same for all specimens. In n -type crystals the Hall effect at first stays negative as the temperature is decreased, but at still lower temperatures it reverses to the same positive value as the p -type samples.

This could be explained thus: The oxygen absorbed on the surface acts as acceptor and produces a surface layer about 5 Å thick containing holes. Calculations of the carrier density and the mobility ($R\sigma$) agree with those observed.

Of course, Mg_2Sn absorbs O_2 strongly and this effect may not be as marked in other substances. But this surface conductivity provides an explanation of the low temperature "intrinsic" conductivity observed in semiconductors with very low density of impurities.

Price: In the case of germanium the experiments by Koenig at Watson Laboratory showed that the impurity band conduction is a genuine bulk transport effect and not surface conduction. The experiments were to compare crystals of different ratios of perimeter to cross section.

Aigrain: Mg_2Sn is unique in that it is the only substance known so far in which the Hall effect changes sign with temperature. I do not think therefore that it is safe to generalize conclusions derived from experiments on this substance alone.

Pines: I should like to tell you something about the information which may be derived concerning impurity conduction by a study of the impurity state spin resonance in n -type Si. The experiments I shall describe have been carried out by George Feher at Bell Telephone Laboratories. What theoretical remarks I shall have to make represent work which has been done at Bell Laboratories this summer by E. Abrahams, P. W. Anderson, and myself.

Suppose we consider the impurity resonance for P-doped Si. At low concentrations ($<10^{17}$) one observes two resonance lines which occur at $\beta H \pm A$, where A is the hyperfine interaction of the electron with the phosphorus

nucleus. These lines correspond to the resonance of electrons with their spins parallel and antiparallel to the spin $\frac{1}{2}$ of the P nucleus. The observed separation is in good agreement with the theoretical calculation by Kohn and Luttinger. At concentrations of the order of 10^{17} P atoms/cc., a third line appears at βH . As Slichter has shown, this represents the expected effect for a cluster of two P atoms, which are so close that their exchange interaction integral is appreciable compared to the hyperfine splitting.

Feher is now able to study the way an impurity spin moves through the solid by looking at one of the lines (say $\beta H - A$) and then, after a given delay time, the other ($\beta H + A$); or alternatively, looking at the one line and then returning to it at a later time. In this fashion he can tell the rate at which a spin changes its environment of Si^{29} nuclei, or goes to a P nucleus of opposite spin, or flips its direction with respect to the external magnetic field.

I first wish to remark that his experiments enable one to put an upper limit on the motion of a given spin, since if a spin moves too fast, one will simply not see the hyperfine-separated lines. (The spin could be at a nucleus with either up or down spin during the time of interest in the experiment.) This upper limit corresponds to an activation energy of the order of a millivolt for spin motion. We are independently led to propose as an explanation for this activation energy the mechanism discussed by Professor Mott yesterday, that is, the Coulomb attraction of the donor and acceptor ions at a compensating center. I might add that we came to the conclusion that compensation must be important because at these low concentrations the transfer integral, K , for the overlap of a donor electron with an adjacent vacant donor site is so very much larger than the exchange integral for two occupied donor sites the same distance apart. We believe the activation energy resulting from the Coulomb attraction may be somewhat less than that mentioned by Professor Mott. If one considers a random array of impurity atoms, the maximum of the distribution function for the nearest neighbor distance lies at $0.88r_s$ (where r_s is the radius of the Wigner-Seitz sphere for an ordered array), while the maximum in the distribution function for next nearest neighbors lies at $1.19r_s$. Thus one could be most likely to encounter an activation energy which is

$$\frac{e^2}{0.88\kappa r_s} - \frac{e^2}{1.19\kappa r_s} \approx \frac{0.32e^2}{\kappa r_s}.$$

Furthermore, because one is dealing with a *distribution* of impurity centers the actual activation energy could be still smaller.

The experiments of Feher at concentrations below 10^{17} donors/cc. tend to substantiate the foregoing picture. First, by measuring the time of motion of a given spin as a function of temperature and concentration he has established the existence of an activation energy which varies roughly as one might expect on the above model. Second, by varying the compensation of his samples he finds that compensation plays an essential role in determining the spin motion, and in one case he has found a relaxation time which is simply proportional to the number of compensating centers.

THE CHEMICAL BOND IN SEMICONDUCTORS

THE GROUP V B TO VII B ELEMENTS AND COMPOUNDS FORMED BETWEEN THEM¹

BY E. MOOSER² AND W. B. PEARSON³

ABSTRACT

A brief review is first given of the developments which led to an understanding of the important role played by chemical bonding in semiconductors. The properties of the Group V B to VII B elements and of some compounds formed between these elements are then considered according to the valence bond model of Pauling. This leads to the conclusion that the band scheme in these substances is somewhat different to that which has been generally accepted, and we discuss the new model in relation to their electrical and optical properties.

1. BRIEF REVIEW OF PREVIOUS WORK SHOWING THE IMPORTANCE OF CHEMICAL BONDS IN SEMICONDUCTORS

In recent years semiconductor research has mainly been carried out along two separate lines: on the one hand new semiconducting materials have been explored and their properties interpreted in terms of a simple band model, the parameters of which were derived from experimental data, while on the other hand much effort has been devoted to deducing the properties of semiconductors theoretically from the properties of the component atoms and the crystal structure. This has led to very promising results in the case of diamond-like semiconductors, and we have at present a rather clear-cut picture of the behavior of the valence electrons in silicon and germanium. However, even in these relatively simple cases our understanding has been reached only by tedious numerical calculations, and it is hard to believe that such calculations will ever lead to a simple theory embracing all semiconductors.

In this situation we see that the valence bond theory as first applied to metals by Pauling (1949) can furnish a straightforward description of semiconductors by establishing a simple connection between the electrical properties and the chemical bonding in solids. The qualitative nature of the valence bond theory prevents it from replacing a careful mathematical analysis of the behavior of the valence electrons in semiconductors. It may, however, suggest new approximations for such an analysis. Moreover, it provides a very useful guide in the search for new semiconducting materials and it is at present the only theory which affords a satisfactory description of amorphous and liquid semiconductors.

The chemical bonding in semiconductors has previously been discussed by various authors. Joffé (1951) pointed out that the short range order, i.e. the chemical bonding, is responsible for the occurrence of semiconductivity in solids rather than a periodic arrangement of the atoms. He emphasized the fact that the bonds in semiconductors and insulators are all saturated as

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opposed to the unsaturated bonds found in metals, thereby indicating that one need not necessarily refer to the band model to distinguish between semiconductors and metals. Welker (1952) succeeded in establishing an empirical relationship between the character of the bonds in semiconductors on the one hand and the charge carrier mobilities and the activation energies on the other hand. This relationship has since been worked out in more detail by Goodman (1955) and put on a theoretical basis by Seraphin (1954) and by Heywang and Seraphin (1956). Krebs and Schottky (1954) have made an attempt to come to a more quantitative understanding of the connection between the chemical bonds in solids and their electrical properties. Finally, the recognition of those features common to the chemical bonding in all semiconductors has led to the definition of a specific "semiconducting bond" (Mooser and Pearson 1956 *a, b, c*).

The concept of a semiconducting bond has provided us with a number of rules with which to predict semiconductivity in substances from their chemical composition and their crystal structure. As a result a number of new semiconductors have been discovered (Mooser and Pearson 1956*d*; Junod, Mooser, and Schade 1956; Busch, Mooser, and Pearson 1956) while Mooser and Pearson (1956*e*) have also given a classification of semiconductors containing tetrahedral sp^3 bonds.

In the present paper we shall apply the concept of the semiconducting bond in discussing the properties of solids containing Group V B to VII B elements only. The present lack of understanding of the conduction mechanism in these substances, as well as the fact that some of them (e.g. Se and Bi_2Te_3) are of considerable technical interest, seems to justify such a discussion.

2. SEMICONDUCTORS CONTAINING GROUP V B TO VII B ELEMENTS ONLY

When we now make use of the concept of the semiconducting bond in considering the properties of elements in the B Groups V, VI, and VII and of compounds containing these elements only, we find that a unified picture can be developed relating the bonding and the conduction mechanism in these substances. The general character of this picture may well relieve many of the rather arbitrary assumptions previously required to explain the properties of specific substances (e.g. selenium).

We will first discuss the Group V elements As, Sb, and Bi; the properties of these are well known, so that the conclusions drawn from our model can readily be checked against the experimental data. Proceeding to the Group VI B elements we next discuss Se and Te. A very considerable amount of experimental data has been collected on these elements; however, it is often conflicting and we cannot give a full account of all the experimental results in the present paper. In the case of compounds few reliable measurements have been made, but such information as we have is also consistent with the model which we propose.

(a) *The Group V B Elements*

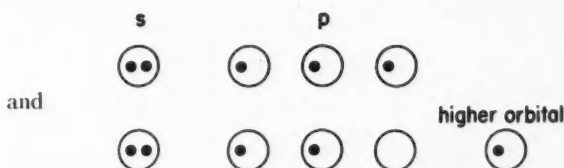
The rhombohedral modifications (A7 type of structure*) of As, Sb, and Bi are generally regarded as obeying the "8-*N* rule"†, each atom having three

*Strukturbericht type of structure.

†See, for instance, Hume-Rothery (1948).

nearest neighbors, and they should, on this basis, contain semiconducting bonds and be semiconductors. This is indeed contrary to their known metallic conduction (Schottky 1955).

Closer examination of the A7 type of structure reveals, as is well known, that the 8-*N* rule is obeyed only approximately. The atoms are arranged in double layers, and while each atom has three nearest neighbors in its own double layer it also has three next-nearest neighbors at only slightly longer distances in the adjacent double layer, resulting in a distorted octahedral coordination of the atoms. This increase of the coordination number in the rhombohedral modifications of As, Sb, and Bi beyond their normal covalency of three is possible through a resonance of the bonds among the six neighboring positions, and it was postulated by Pauling (1919) that such a resonance necessitates the presence of empty orbitals in the valence shells of some atoms. The valence states of rhombohedral As, Sb, and Bi must therefore be considered as a combination of



one electron being promoted into a higher orbital in the latter configuration. The empty *p* orbital as well as the electron in the higher orbital then gives rise to the metallic properties found experimentally.

It is significant that both As and Sb also exist in amorphous modifications which show semiconducting properties (see e.g. Moss 1952). Small regions of double layers similar to those found in the rhombohedral form are still present in the amorphous modifications; however, in the amorphous form the layers are randomly arranged with respect to one another (Krebs, Schultze-Gebhardt, and Thees 1955; Krebs and Schultze-Gebhardt 1956). This random arrangement results in an increase of the average next-nearest neighbor distances from $r_2 = 3.15 \text{ \AA}$ in crystalline As to $r_2' = 3.75 \text{ \AA}$ in amorphous As, the corresponding values for Sb being $r_2 = 3.37 \text{ \AA}$ and $r_2' = 3.75 \text{ \AA}$. The increased next-nearest neighbor distances are consistent with the disappearance of resonances involving higher orbitals as the atoms are no longer six-coordinated. In fact a true three-coordination is found in the amorphous forms and they obey the 8-*N* rule, so that the conditions for the occurrence of semiconducting bonds are indeed fulfilled.

Using this valence bond picture as a guide we can now interpret the properties of the Group V elements in terms of a simple band model. It follows from the semiconducting properties of amorphous As and Sb that the band structure of these elements consists of two separated bands, a filled valence band and an empty conduction band. In As these bands are separated by 1.2 eV, while in Sb the separation is only of the order of 0.1 eV. (see e.g. Moss 1952). The bands obviously arise from the special arrangement of the atoms in the double layers and as these double layers are also found in the rhombohedral modifi-

cations, we expect the bands to be only slightly affected by the transition from the amorphous to the crystalline state. However, the drastically decreased next-nearest neighbor distances in the crystalline forms lead to a considerable overlap of higher atomic orbitals. We suggest that these overlapping orbitals are *d*-orbitals as their symmetry fits rather well with the near octahedral coordination of the atoms. Because of the overlapping the energy band corresponding to these orbitals is rather broad and its lower edge dips into the valence band, thereby bridging the energy gap and giving rise to the metallic properties actually observed.

It is of interest to note that on going from amorphous As to amorphous Sb the separation between valence and conduction band decreases from 1.2 ev. to 0.1 ev. By extrapolation one would therefore expect the corresponding bands in Bi to overlap and it is not astonishing that no semiconducting phase of Bi is known. In fact, amorphous films of Bi exhibit superconducting properties below 6° K. (Hilsch and Barth 1955).

The difference of the band scheme of Bi as opposed to that of Sb and As may also be responsible for the observed differences in the de Haas - van Alphen effect of these substances. While short period dependences of the magnetic susceptibility upon the reciprocal magnetic field are found in As and Sb, only a long period dependence is observed in Bi* (see e.g. Steele 1955; Berlincourt 1955).

(b) *The Group VI B Elements*

The hexagonal, A8 type of lattice of Se and Te consists of spiral chains which are arranged in such a way that, in addition to the two nearest neighbors lying in the same chain, each atom has four next-nearest neighbors in adjacent chains. As in As, Sb, and Bi the atoms thus acquire a distorted octahedral coordination. The distances between next-nearest neighbors are too short to be due to van der Waals bonds only, and one is again led to the assumption of resonating bonds (see e.g. von Hippel 1948), some of the valence electrons being promoted to higher orbitals. However, because of the different electronic structure of Se and Te the resonances are considerably less pronounced in these elements than in those of Group V B. This is readily recognized from the increased ratio of next-nearest to nearest neighbor distances found in Group VI B (see Table I). As a result the resistivities of Se and Te are rather

TABLE I

	r_2/r_1		r_2/r_1
As	1.25	Se	1.49
Sb	1.17	Te	1.31
Bi	1.12	(Po)	1.0

high and both elements are usually considered to be semiconductors. However, the occurrence of resonating bonds involving higher orbitals suggests that the energy gap found from the electrical and optical properties is in fact bridged

*In the case of As both long and short period dependences are found.

by a band of low state-density. This band overlaps the valence band and thus gives rise to a small and temperature independent number (10^{14} – 10^{16} cm.⁻³) of free charge carriers in both Se and Te. The band model suggested here is supported by a quantitative analysis of the band structure of Se given by Noguchi (1954)* who finds an overlap of the conduction and the valence bands in certain regions of k -space.

In interpreting some of the experimental data in terms of the present model we first note that both Se and Te are p -type conductors (in pure Te n -type conduction is observed at elevated temperatures) regardless of whether the substances are pure or doped with various impurities (see e.g. Henkels and Maczuk (1954) for Se and Kronmüller, Jaumann, and Seiler (1956) for Te). If we assume the electrons in the overlapping band (i.e. the electrons in higher orbitals) to have a small mobility, then this behavior is readily understood with our model, since because of the overlap the valence band always contains some free holes. Moreover, the resonance bonds between chains are strongly affected by lattice imperfections. Such imperfections may in fact destroy the resonances throughout extended regions of the crystal, thereby reducing the number of free charge carriers considerably. It is therefore not astonishing that heat treatment has a pronounced influence on the resistivity of Se (see e.g. Schweickert (1955); for a list of recent experimental work on Se see also Brunke (1955)). It is significant that the apparent activation energy as determined from electrical measurements decreases with increasing annealing time, indicating that the better the perfection of the lattice, the more the charge carrier density becomes independent of temperature (Henkels 1951; Plessner 1951). This is in good accord with the expected onset of resonances as the chains get more and more perfectly arranged throughout the lattice.

A somewhat similar effect was observed by Henkels and Maczuk (1954) on doping Se with insoluble impurities. The distortion of the chains due to such impurities destroys some of the resonating bonds. The number of free charge carriers is thus reduced and the resistivity increased, the effect being bigger for impurity atoms with large radii.

In the amorphous modification of Se, and also in liquid Se, the spiral chains of the hexagonal phase are still present. However, because of the random arrangement of the chains with respect to one another all resonances are destroyed. The overlapping of the bands disappears and one does indeed find true semiconducting properties in these phases (Henkels and Maczuk 1953, 1954). It is remarkable that absorption measurements on both amorphous and hexagonal Se show an absorption edge at about the same wavelength (see e.g. Moss 1952), indicating that the valence and conduction bands of amorphous Se are essentially preserved in the crystalline modification. However, in the long wavelength region the absorption constant of hexagonal Se is about 10^3 times larger than that of amorphous Se, and we believe that this high absorption constant is due to the third band bridging the forbidden energy zone.

*Unfortunately Noguchi's paper was accessible only in abstracted form.

The experimental data on Te are easier to assess and in fact most of them can be interpreted with simple semiconductor theory. This is to be expected, since the energy gap between the valence band and the next higher *non-overlapping* band is only 0.35 eV., and at temperatures around or above room temperature some electrons will be excited across this gap in spite of the presence of a third overlapping band with a low density of states. However, there are some results which are not understood on the basis of semiconductor theory. As mentioned earlier, Te always shows *p*-type conduction at low temperatures, becomes *n*-type in what is usually called the intrinsic range, and at even higher temperatures is again *p*-type. This behavior has been explained by assuming a temperature dependent number of lattice defects (Fritzsch 1952). The "three-band-model" readily suggests an alternative interpretation. However, because of the qualitative nature of our model such an interpretation is not free of ambiguity, and detailed knowledge of the actual band structure is called for to furnish a proper solution of the problem. Further experimental evidence for the existence of an overlapping band is furnished by the high absorption constant of Te in the far infrared region (see e.g. Moss 1952). Finally we may mention that, as in the case of Se, liquid Te also shows semiconducting properties (Epstein and Fritzsch 1954).

Unlike Se and Te, α -Po has a cubic structure in which each atom is exactly octahedrally surrounded by six neighbors. The resonances are fully developed here and Po therefore shows metallic properties.

(c) *Compounds Formed between Group V B to VII B Elements*

In the case of compounds between Group V B to VII B elements the situation is somewhat more involved. The fact that the 8-*N* rule is not strictly obeyed in such a compound need not be due to the occurrence of resonances involving higher orbitals, since here electron transfer processes can lead to empty orbitals in the *s* and *p* subshells. However, there exists a number of compounds whose crystal structures still suggest the presence of resonances involving higher orbitals. In the C33 type of lattice found in Bi_2Se_3 multiple layers are formed which consist of five monatomic layers in the sequence Se, Bi, Se, Bi, Se. The coordination of the bordering Se atoms is very similar to that of the atoms in the rhombohedral structure of the Group V B elements. Each Se has three Bi neighbors in the same multiple-layer and three next-nearest Se neighbors in the adjacent multiple-layer. The resonances leading to such a coordination again require the promotion of electrons into higher orbitals and it is found experimentally that Bi_2Se_3 as well as the isomorphous Bi_2Te_3 shows a metallic temperature dependence of the resistivity (Moser and Pearson 1956d; Goldsmid 1956). As in the case of Se and Te the presence of an overlapping band with low state-density, which leads to a metallic temperature dependence of the electrical conductivity in these compounds, does not prevent the observed optical excitation into what is usually called the conduction band (Gibson and Moss 1950).

The D_{5h} structures of Sb_2S_3 , Sb_2Se_3 , and Bi_2S_3 and the D_{0h} structures of AsI_3 , SbI_3 , and BiI_3 probably involve a similar resonance mechanism.

It is significant that the A_2B_3 compounds discussed above all choose the $C33$ or $D5_8$ types of structure rather than the $D5_3$ or $D5_9$ types adopted by compounds containing Group II B and Group V B elements; in the latter the divalent metal contains vacant orbitals in the valence shell which can be used for pivotal resonance, no electron promotion into higher orbitals being necessary. The $D5_3$ and $D5_9$ structures can be regarded as defect forms of the fluorite lattice, and II-V compounds such as Zn_3P_2 are true semiconductors.

3. CONCLUSION

If Pauling's postulate of the need of a vacant orbital in the valence shell for pivotal resonance to occur is true, then it seems inescapable that, in the Group V B and VI B elements and their compounds with each other which we have discussed, they must make use of higher orbitals in the bond scheme, since the coordination of each of the component atoms in these substances exceeds its normal covalency. The valence band in these substances must therefore be overlapped, but in the lighter elements such as As, Sb, Se, and Te the optical properties indicate that the overlapping band is not that usually referred to as the conduction band. It is our hypothesis that the overlapping band (which may overlap the valence band in certain directions only) is derived from the next higher (i.e. d) atomic orbitals and that any interpretation of the electrical properties of these substances must take the presence of this band into account. We find that these new considerations are not in disagreement with the observed properties of those elements; in fact, in many cases they relieve the arbitrary assumptions which had previously been made to explain their properties.

We believe the same picture to hold in the case of compounds formed between these elements, provided that the average atomic number is not too large; however, at present there is little useful experimental data on pure substances with which to test our hypothesis.

In the case of the heavier elements Bi and Po the conventional conduction band appears to have overlapped the valence band. This is certainly the case with α -Po, which is a true metallic conductor and which has a different crystal structure to Se and Te. The absence of an amorphous form of Bi with semiconducting properties, together with other differences in the properties of Bi and of As and Sb, points to a similar situation occurring in Bi.

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DISCUSSION OF THE PAPER OF MOOSER AND PEARSON

Sondheimer: I should like to know how your concept of the semiconducting bond applies to a semiconductor like anthracene.

Mooser: To a first approximation anthracene is made up of isolated molecules with discrete energy levels. However, the interaction between the molecules is large enough for these levels to be split into narrow bands, which do not overlap, and therefore semiconducting properties can arise. In previous papers we have excluded molecular crystals from our discussions because of their low conductivity; but it is clearly a matter of convention whether one regards them as semiconductors or insulators. The semiconductivity of anthracene certainly does not conflict with the concept of the semiconducting bond, but it would not be possible from this concept to predict which molecular crystals show appreciable electronic conduction.

GALVANOMAGNETIC EFFECTS IN *n*-TYPE InSb AT 4.2° K.¹

BY H. P. R. FREDERIKSE² AND W. R. HOSLER

The Solid State Physics Section of the National Bureau of Standards is engaged in a research program on the electrical, optical, thermal, and mechanical properties of semiconducting compounds.

During an investigation of the galvanomagnetic effects in *n*-type InSb at helium temperatures, it was found that the magnetoresistance shows a sinuous character (Fig. 1) similar to that observed in Bi and several other metals. (The analogous behavior in the susceptibility of these metals is known as the *de Haas-van Alphen* effect.)

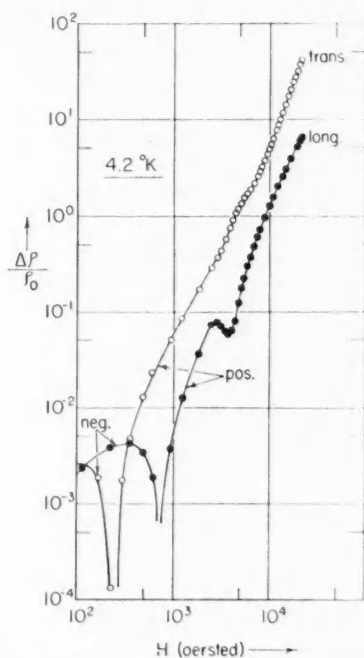


FIG. 1. Magnetoresistance of *n*-type InSb at helium temperatures.

The theory of the magnetoresistance has been treated by Davydov and Pomeranchuk (1) with special reference to Bi. The oscillatory effects are due to a quantization of the electron orbits in a magnetic field. These oscillations can be observed if the condition $\omega_c \tau > 1$ is fulfilled. (τ = collision time, ω_c =

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cyclotron resonance frequency = eH/m_e^*c , H = magnetic field strength, m_e^* = effective mass.) The authors have shown that a minimum in the resistance will occur when

$$(1) \quad \zeta = (n + 1/2)\hbar\omega_c,$$

where ζ = Fermi energy and $n = 0, 1, 2, \dots$

The particular sample of InSb under investigation had an electron concentration of 1.1×10^{15} per cc. as deduced from Hall effect measurements. Owing to the small (and isotropic) effective mass ($m_e^* = 0.013 m_e$ from cyclotron resonance experiments (2)) the electron gas is degenerate and the impurity band can be considered to have merged completely with the conduction band. The calculation of the Fermi energy is now very simple. Eq. (1) predicts then a resistance minimum for $n = 0$ at 3400 oersteds in very good agreement with the measured value. The negative magnetoresistance in the region between 10^2 and 10^3 oersteds is as yet unexplained.

A subsequent investigation of the Hall effect as a function of the magnetic field at 4.2° K. showed a rather constant Hall coefficient up to 12,000 oersteds, followed by a steep increase at higher fields. Such a behavior can be explained as follows. In zero magnetic field the effective Bohr radius is very large (in this case about 600 Å); the wave functions of electrons on adjacent impurities overlap and the resulting impurity band has a width appreciably larger than the donor activation energy. A magnetic field, however, will decrease the effective Bohr radius and diminish the width of the impurity band. At a sufficiently high field this band will separate from the conduction band and some of the conduction electrons will be deionized, causing a rise of the Hall coefficient ("freeze-out") (2).

It has been possible to re-excite electrons into the conduction band by increasing the electric field across the sample, when the specimen was held in a magnetic field of 22,000 oersteds. This observation could be interpreted as a gradual breakdown effect.

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ELECTRON INTERACTION IN SOLIDS¹

BY DAVID PINES²

I. INTRODUCTION

The problem of electron transport in metals is essentially that of the way in which an assembly of particles which interact strongly with one another responds to the action of relatively weak external fields. It is not surprising that the pioneering treatments of electron motion in metals ignored the complications raised by the Coulomb interaction between the electrons and dealt with an independent particle model for electron transport, that is with the motion of a single electron moving in a periodic lattice disturbed by sound waves, imperfections, and the like. Such a model is mathematically tractable. It can also be made plausible on physical grounds. Perhaps most important, in the hands of Bloch, Bardeen, and others it led to predictions which are in good qualitative and fair quantitative agreement with experiment. It is not, however, a consistent theory. As soon as one tries to include the effects of electron interaction, as evidenced through electron-electron scattering, or, say, the alteration of the one-electron energies resulting from exchange contributions, the foregoing agreement disappears. This disappearance is in some cases even associated with a divergence of the calculation in question. In other words, the extreme single electron model works—but any attempt to improve it within the framework of a one-electron approach ends in disaster.

Recently it has appeared possible to develop a consistent independent electron model, in the sense that the interaction between the electrons may be taken into account and shown to be small. Bohm and I (1), starting from a many-electron approach to the free electron gas, have shown that the consequences of the Coulomb interaction are twofold. First, long-range correlations in the motion of the electrons do occur. They give rise to an organized oscillation of the system as a whole, which is the quantum analogue of the classical plasma oscillation observed in gaseous discharges. Second, the electron-electron interaction is screened, with an effective radius of the order of the average inter-electron spacing. The plasma oscillations have a very high frequency so that the lowest energy plasmon (plasma quantum) has an energy greater than the energy of an electron at the top of the Fermi distribution. As a result plasmons are not excited under normal circumstances, and the only role of the Coulomb correlations is the screening action which makes an independent particle model consistent. For with the screened interaction, the influence of electron interaction on a wide variety of metallic phenomena may be computed and shown to yield only relatively small corrections to properties calculated neglecting that interaction (cf. SSP(1)).

The foregoing considerations apply to the free electron gas model for a

¹Presented at the International Conference on Electron Transport in Metals and Solids, held in Ottawa at the National Research Laboratories, September 10-14, 1956.

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metal in which the ion core potential is replaced by a uniform background of positive charge. One might ask—to what extent are the conclusions drawn from the free electron gas model affected by the actual periodic potential encountered in a metal? It is clear that the influence of individual electron intra-band transitions on the plasmon spectrum is well described by a free electron gas model. However, the consideration of inter-band transitions lies beyond the scope of the free electron approach, and so it is with their effect on the plasmon spectrum and the effective electron-electron interaction that we will be concerned. We shall see that for most metals the inter-band transitions do not appreciably alter the conclusions drawn from the study of the free electron gas model. Mott provided us with the essential clue in this regard two years ago at the Solvay Congress (2). He showed that inter-band transitions might only be expected to influence the free electron plasma spectrum if the matrix elements for an individual-particle transition to an excited state in the vicinity of or greater than the plasmon energy were large, a situation which does not obtain for most metals. Mott derived this result by semiclassical arguments. Kanezawa (3) has given a quantum treatment of this problem which leads to identical results for the plasmon energy.

Recently, Nozières and I (4) have considered the general formulation of electron-electron interaction in solids. We have been interested in generalizing the results of Kanezawa to include the influence of the core electrons on valence electron motion, and in deciding what the effective electron-electron interaction will be for any kind of solid. I shall begin by giving a brief summary of our method and results. I shall also report briefly the experimental results, which indicate that the inter-band transitions have only a slight influence on the plasmon excitation spectrum not only for most metals but for nearly all other solids (insulators, semiconductors, compounds, etc.).

I should then like to apply these results to the consideration of the influence of electron-electron interaction on electron transport in metals and semiconductors. I shall consider four ways in which this influence might be felt:

- (1) Direct electron-electron scattering in metals.
- (2) The role of electron interaction in determining the effective electron-phonon interaction in metals.
- (3) The alteration of the one-electron energy spectrum in metals.
- (4) The existence of other elementary excitations (apart from electrons, phonons, high frequency plasmons) which might then serve to scatter electrons and phonons.

II. THE FORMAL TREATMENT OF ELECTRON-ELECTRON INTERACTION IN SOLIDS

The approach given in NP(4) for electron-electron interaction in solids is directly analogous to that used in BP(1) for the free electron gas. Let us consider only the valence electrons (electrons outside the closed shells of the individual atoms) explicitly, and assume that influence of the core electrons may be well described by a potential. We introduce a set of extra co-ordinates (the plasmon variables) to describe the plasma oscillations of the valence electrons, and then

redescribe the long-range part of Coulomb interaction between the valence electrons in terms of the plasmons. The basic Hamiltonian may then be written as follows:

$$\begin{aligned}
 (1) \quad H = & \sum_i \left(\frac{p_i^2}{2m} + V(r_i) \right) + \sum_{i \neq j, k > k_c} \frac{2\pi e^2}{k^2} \exp[ik \cdot (x_i - x_j)] \\
 & + \sum_{k < k_c} \left(\frac{P_k P_k}{2} + \frac{\omega_p^2 Q_k^* Q_k}{2} \right) \\
 & + \sum_{k < k_c} \left(\frac{4\pi e^2}{k^2} \right)^{\frac{1}{2}} \left(\frac{k \cdot p_i}{m} - \frac{\hbar k^2}{2m} \right) Q_k \exp(ik \cdot x_i) \\
 & + \sum_{\substack{ik, l < k_c \\ k \neq -l}} \frac{2\pi e^2}{m} \frac{k \cdot l}{|k||l|} Q_k Q_l \exp[i(k+l) \cdot x_i]
 \end{aligned}$$

provided we impose a set of supplementary conditions on our extended system wave function,

$$(2) \quad \left[P_k - i \left(\frac{4\pi e^2}{k^2} \right)^{\frac{1}{2}} \sum_i \exp(ik \cdot x_i) \right] \psi = 0 \quad (k < k_c).$$

The first three terms in (1) describe the valence electrons moving in the periodic potential of the ion-cores and interacting via a short-range interaction. The next two describe the plasmon field, with coordinates Q_k and momenta P_k ; we have introduced $n' = k_c^3/6\pi^2$ plasmon degrees of freedom. The plasmons have a frequency

$$(3) \quad \omega_p = (4\pi n e^2/m)^{\frac{1}{2}}$$

where n is the density of valence electrons. The remaining terms represent a linear and non-linear plasmon-electron interaction respectively. In cases such that the linear interaction may be regarded as small (an essential condition to the success of the method) the non-linear interaction is very much smaller. We neglect it in what follows.

We now wish to obtain the eigenfunctions and eigenvalues for the Hamiltonian (1). At this stage our treatment differs from that of BP only in the appearance of $V(r_i)$ in the Hamiltonian (1). We are particularly interested in the way in which this term influences the plasmon-electron coupling, since our ability to work with the Hamiltonian (1) hinges upon our ability to treat the effect of this interaction on the electron and plasmon motion. In the absence of the plasmon-electron interaction, the electrons should be well described by the set of Bloch waves ψ_k , which are the eigenfunctions of the one-electron Hamiltonian, $(p_i^2/2m) + V(r_i)$. We have

$$(4) \quad [(p_i^2/2m) + V(r_i)] \psi_k(r_i) = E_k \psi_k(r_i).$$

It turns out that the electron-plasmon coupling will be weak provided the important part of the one-electron excitation spectrum described by (4) lies well below the plasmon spectrum. By important part, I mean that set of excited states for which the oscillator strengths or density fluctuation matrix elements from the ground state are appreciable.

Expressed mathematically, the foregoing criterion for weak plasmon-electron interaction reads

$$(5) \quad \omega_{on}^2(k)/\omega^2(k) \ll 1$$

where $\omega_{on}(k)$ is an excited one-electron state of momentum k above the ground state, and $\omega(k)$ is the frequency of a plasmon with momentum k . If we work in the reduced zone scheme, we may write

$$(6) \quad \hbar\omega_{on}(k) = E_{s+K+k} - E_s = \hbar\omega_{sK}(k)$$

where K is a reciprocal lattice vector; $K = 0$ corresponds to an intra-band transition, $K \neq 0$ to an inter-band transition. The condition (5) applied to intra-band transitions is in general quite well satisfied for metals. In this case, ω_{on}^2/ω^2 is essentially the free electron plasmon-electron coupling constant, being approximately $k^2\langle v^2 \rangle_{AV}/\omega^2$, where $\langle v^2 \rangle_{AV}$ is the mean square electron velocity. As shown in SSP, the condition (5) is then very well satisfied for all plasmon momenta, k . For the valence electrons in a semiconductor or an insulator it is trivially satisfied, there being no intra-band transitions because of the Pauli principle. Whether the important inter-band one-electron excitations have a low-lying spectrum cannot, of course, be answered in general, but a good guide is the size of the gap between the occupied bands and the nearest unoccupied bands. Where this is small compared to $\hbar\omega$, as is the case for most metals and for the valence electrons in a semiconductor, the low-lying excited states will predominate, and the electron-plasmon interaction will be weak. Where the gap is large, as is the case for some insulators, or where the "d" shell plays an important role, as is the case for the transition metals and those just beyond them in the periodic table, the one-electron excitation energies are comparable with the plasmon energies, and the simple picture we now describe does not apply.

The linear plasmon-electron interaction gives rise to two effects: a shift in the plasmon spectrum, and an effective electron-electron interaction. Its influence may be taken into account by carrying out a canonical transformation which eliminates the interaction to first order. The transformation may be conveniently carried out if one works in a mixed representation in which the plasmon operators are treated explicitly, and the electron operators are defined through their matrix elements between the Bloch waves (4). The results, which are equivalent to those obtained by Kanezawa, are the following:

(1) The new plasmon frequency ω is defined by the dispersion relation

$$(7) \quad 1 = \frac{4\pi e^2}{m} \sum_{sK} \frac{f_{sK}}{\omega^2 - \omega_{sK}^2}$$

where the f_{sK} are the oscillator strengths for the valence electron intra-band and inter-band transitions, and the ω_{sK} are the analogous frequency differences defined through (6). We have suppressed the dependence of f_{sK} and ω_{sK} on k , the momentum above the ground state of the individual electron (or plasmon) excitation we are considering. The dispersion relation (7) is just that derived by Mott.

(2) The matrix elements for the effective electron-electron interaction are given by

$$(8) \quad (H_{\text{eff}})_{mn,pq} = \sum_{k < k_c} \frac{2\pi e^2}{k^2} \frac{\omega_{mn}(\rho_k)_{mn} \omega_{pq}(\rho_k^*)_{pq}}{\omega^2 - \omega_{pq}}.$$

In (8) the labels q, n correspond to any pair of one-electron states κ, κ' while p, m correspond to the states $\kappa + k + K_n, \kappa' - k + K_m$, where K_n, K_m are any pair of reciprocal lattice vectors.

(3) The subsidiary conditions now act only on the electrons. If the state function Ψ for the electrons is expanded in terms of determinants Φ_n formed from the Bloch functions,

$$(9a) \quad \Psi = \sum_n a_n \Phi_n,$$

then the subsidiary conditions are

$$(9b) \quad \sum_n \frac{\omega^2}{\omega^2 - \omega_{mn}} (\rho_k)_{mn} a_n = 0 \quad (k < k_c)$$

for all states m . Since the ρ_k connect only one-electron states, the $(\rho_k)_{mn}$ and ω_{mn} are really various one-electron matrix elements and frequency differences.

We now remark that where $\omega_{mn}^2 \ll \omega^2$, the above results simplify considerably, and reduce, in fact, to those obtained for the free electron gas. Thus we find that the dispersion relation, (7), becomes, by the f sum rule,

$$(10) \quad 1 \cong \frac{4\pi e^2}{m} \sum_{\kappa K} \frac{f_{\kappa K}}{\omega^2} = \frac{4\pi n e^2}{m \omega^2}.$$

Furthermore the long-range part of the Coulomb interaction may be neglected, since H_{eff} will now have matrix elements which are very much smaller than those originally present in the Coulomb interaction, i.e.

$$(H_{\text{eff}})_{mn,pq} \ll \sum_{k < k_c} \frac{2\pi e^2}{k^2} (\rho_k)_{mn} (\rho_k^*)_{pq}.$$

Finally the subsidiary conditions, (9b), reduce to the approximate free electron expressions

$$\rho_k \psi = 0 \quad (k < k_c).$$

Thus where the one-electron excitation spectrum lies below the plasmon spectrum, the electron interactions may be treated in just the same way as for the free electron gas, and we need consider only an effective screened interaction, $H_{s,r}$, if we are interested in computing the role of electron interaction in various phenomena in solids.

Fortunately we do not have to rely solely on our theoretical expectations in deciding whether the plasmon-electron interaction is in fact weak for a given solid. Instead we can use the experiments on plasmon excitation in solids to serve as a guide to whether the foregoing simple picture applies. Plasmons will be excited when an external fast charged particle passes through the solid. Their excitation is most commonly observed by studying the energy loss spectrum of kilovolt electrons emerging in the forward direction ($< 10^{-2}$

rad. scattering) from solid films of several hundred Å thickness. As was first discovered by Ruthemann (5) and Lang (5) the electrons give up energy in multiples of a basic quantum—the plasmon, in most cases. A detailed summary of the theoretical and experimental evidence for plasmon excitation in solids has been given elsewhere (6) and we here merely reproduce in Tables I–III several tables which compare the observed energy losses with the free electron plasmon energy. The experimental values quoted in Tables I and II represent an average of the results of a number of investigators. We note that where we expect that $\omega_{en}^2 \ll \omega^2$, it is (Table I), and where this condition should not be satisfied, it is not (Table II). What is at first sight surprising is that this criterion is well satisfied for such a wide variety of compounds (Table III). We further remark that those cases in Table II for which there is agreement between the observed energy loss and $\hbar\omega_p$ probably represent a cancellation of contributions with $\omega_{en} > \omega_p$ and $\omega_{en} < \omega_p$, as discussed in Reference 6.

TABLE I

A COMPARISON OF $\hbar\omega$ WITH ΔE_{obs} FOR SOLIDS IN WHICH THE VALENCE ELECTRONS ARE WEAKLY BOUND ($\omega_{en}^2 < \omega^2$) (AFTER PINES (6)): z DENOTES THE NUMBER OF VALENCE ELECTRONS PER ATOM WE HAVE ASSUMED TAKE PART IN PLASMA OSCILLATION

	Be	B	C	Mg	Al	Si	Ge
z	2	3	4	2	3	4	4
$\hbar\omega$ (ev.)	19	24	25	11	16	17	16
ΔE_{obs} (ev.)	19	19	22	10	15	17	17

TABLE II

A COMPARISON OF $\hbar\omega$ WITH ΔE_{obs} FOR SOLIDS FOR WHICH THE VALENCE ELECTRONS ARE NOT WEAKLY BOUND (AFTER PINES (6)): z DENOTES THE NUMBER OF VALENCE ELECTRONS PER ATOM WE HAVE ASSUMED TO TAKE PART IN PLASMA OSCILLATION

	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn
z	4	6	7	8	9	10	11	12
$\hbar\omega$	17	24	28	31	34	35	36	32
ΔE_{obs}	22	24	22	21	21	23	20	23
	Se	Mo	Pd	Ag	Cd	In	Sn	Sb
z	6	6	10	11	12	3	4	5
$\hbar\omega$	18	23	31	30	28	11	12	14
ΔE_{obs}	20	25	22	23	20	12	12	15
	Te	Ta	W	Pt	Au	Tl	Pb	Bi
z	6	5	6	10	11	3	4	5
$\hbar\omega$	15	20	23	30	30	12	13	14
ΔE_{obs}	18	21	22	23	24	17	13	13

TABLE III

A COMPARISON OF $\hbar\omega$ WITH ΔE_{obs} FOR COMPOUNDS: z DENOTES THE AVERAGE NUMBER OF VALENCE ELECTRONS PER ATOM WE ASSUME TAKE PART IN PLASMA OSCILLATION (AFTER PINES (6)) (THE INVESTIGATORS ARE MARTON AND LEDER (ML), WATANABE (W), AND MOLLENSTEDT (M))

	ZnS	PbS	Sb ₂ S ₃	MoS ₂	PbTe	PbSe	Mica	BeO	MgO
z	4	5	5.6	6	5	5	4.7	4	4
$\hbar\omega$	17	16	18	23	14	15	24	29	25
ΔE_{obs}	17	15	19	21	15	15	25	29	25
Investigator	ML	ML	ML	M	ML	ML	M	W	W

	Li ₂ CO ₃	Ca(OH) ₂	MoO ₃	SiO ₂	Al ₂ O ₃	TeO ₂	SnO ₂	KBr	KCl	NaCl
z	4	3.2	6	5.3	4.8	6	5.3	4	4	4
$\hbar\omega$	24	21	24	25	27	23	26	13	14	16
ΔE_{obs}	24	22	25	25	23	18	20	13	13	16
Investigator	W	W	W	W	W	ML	W	ML	ML	ML

III. THE INFLUENCE OF ELECTRON INTERACTION ON ELECTRON TRANSPORT IN METALS

We now turn to some of the ways in which electron interaction influences electron transport in metals. We shall use the free electron model for our calculations, since as we have seen it should provide quite an accurate model for a wide variety of metals. Thus we shall take the screening length λ_c for the electron-electron interaction as given by the free electron value (cf. SSP),

$$\lambda_c \cong 1.4 r_s^{1/2} a_0$$

where r_s is the inter-electron spacing measured in units of the Bohr radius ($4\pi r_s^3 a_0^3/3 = 1/n$). λ_c is clearly of the order of the inter-electron spacing.

A. Electron-Electron Scattering

It is obvious that if the effective electron interaction were not screened, metals would behave quite differently. It is the screening, combined with the Pauli principle, which reduces the effectiveness of the direct electron-electron scattering to the point that it may be neglected vis-à-vis the electric-phonon scattering except at very low temperatures. Abrahams (7) has calculated the cross-section for electron-electron scattering for the free electron gas, under the quite reasonable assumption that $H_{e,r}$ may be represented by a repulsive Yukawa interaction,

$$H_{e,r} \cong (e^2/r) \exp(-k_c r).$$

For this interaction the Born approximation is not valid, and a partial wave analysis is required. Abrahams finds a mean free path L for electron-electron scattering, which is

$$(11) \quad \frac{1}{L} \cong \frac{4\pi}{k_c^2} n \left(\frac{kT}{E_F} \right)^2.$$

The dependence of the expression, (11), on kT/E_F arises from the restrictions

on momentum transfer introduced by the Pauli principle (cf. Jones, Ref. 7). For sodium one finds that L becomes as short as the electron-phonon mean free path only at $\sim 4^\circ \text{K.}$, where both are $\sim 2.5 \text{ cm.}$ Thus we should require extremely pure samples in order to be able to detect the influence of electron-electron scattering, since the mean free path for impurity scattering is usually considerably less than 2.5 cm. It is possible that one might be able to detect an effect associated with the direct scattering on a metallic sample with less than 10^{15} – 10^{16} impurities/cc.

Actually in order for electrical conductivity to be affected, we require that the current be altered. This in turn occurs only if an effective momentum transfer to the lattice takes place. The current may be altered by electron-electron collisions in two ways: by Umklapp electron-electron scattering; or because the electron energy surfaces are highly anisotropic, so that one essentially considers collisions between electrons of different effective masses (8). In the former case, the cross-section will be smaller and the mean free path somewhat longer for an electron-electron U-process, since the matrix elements are necessarily reduced. A crude estimate indicates the reduction could amount to a factor of k_c^2/K^2 where K is a low-lying reciprocal lattice-vector. This yields a reduction factor between one-half and one-fourth. For the anisotropic electron energy surfaces, the cross-section should be of the same order of magnitude as that calculated for the free electron gas.

The electron-electron collisions may also alter the thermal conductivity. Very roughly, we might expect to find a contribution to the thermal resistance which is

$$W_{e.e.} = \frac{1}{K_{e.e.}} = \frac{1}{c_e v_0 L} = \frac{1}{n} \left(\frac{E_F}{kT} \right) \frac{1}{v_0} \frac{4\pi}{k_c^2} n \left(\frac{kT}{E_F} \right)^2;$$

$$W_{e.e.} \approx \frac{4\pi}{k_c^2} \frac{1}{v_0} \left(\frac{kT}{E_F} \right).$$

It should be added that we do not require U-processes for electron-electron collisions to contribute to thermal resistance.

There is also the possibility of the scattering of s electrons by d electrons in the transition metals. This was calculated by Baber (9) some time ago, and there is some experimental evidence for a T^2 temperature dependence in the resistivity of Pd.* As I have mentioned, it has thus far not been possible to treat in detail the electron-electron interaction in the transition metals. Speaking qualitatively, it seems likely that the " s "–" s " and " s "–" d " electron interactions are screened, with a radius of the order of the inter-electron spacing, while the " d "–" d " interactions are much less affected. There is clearly a need for much more work in this direction.

B. Electron-Phonon Interaction

The influence of the electron interaction on the electron-phonon interaction in metals has already been discussed at this conference by Professor Bardeen

*See Reference 9, and the reports by K. Mendelssohn and G. K. White at this conference.

(10). Here I wish only to remind you of the general physical picture which obtains and the results one finds (11). Because the ions in a metal are heavy and slow, when they move the conduction electrons respond easily to that motion and very nearly cancel out the ionic fields. As a result the field which acts on a given electron must be taken as that due to the ionic motion plus that arising from the screening action of the other conduction electrons. It turns out that, for practical purposes, one can get a good estimate of the effective electron-ion interaction by taking the interaction to be of the form $[Ze^2/|r_i - R_0|] \exp[-|r_i - R_0|/\lambda_c]$ where λ_c is the Fermi-Thomas screening radius, $v_0/\sqrt{3}\omega_p$ (v_0 is the velocity of an electron at the top of the Fermi distribution). The electron-electron and electron-phonon interactions also determine the phonon spectrum in a metal. If the ions are regarded as point charges and the electron-ion and electron-electron interactions are neglected, the phonon frequency for long wavelengths is nearly constant, and is given by the ionic plasma frequency,

$$\Omega_p = (4\pi NZe^2/M)^{1/2}$$

where N , Z , and M are the ionic density, charge, and mass. As a consequence of the electron screening action, the effective ion-ion interaction is screened, with a radius $\sim \lambda_c$, and the sound wave frequency is altered to

$$\Omega \sim kv_0\Omega_p/\sqrt{3}\omega_p.$$

The latter expression yields good qualitative agreement with experiment. We shall discuss later the possibility of somewhat similar behavior arising from the electron-hole interaction in a semiconductor.

C. Alteration of the One-electron Energy Spectrum

The energy spectrum of the one-electron excitations in a metal will be changed from its free electron value as a consequence of electron-electron interaction. As we shall see, the changes involved are comparatively small, amounting to corrections of the order of 10–20%. That the influence of electron-electron interaction is so slight may again be traced to the combination of electron correlation, which leads to screening, and the Pauli principle, which prevents the short-range interaction, $H_{s.r.}$, from influencing the energy spectrum appreciably. Thus if we had only the Pauli principle, we would be in serious difficulties, since the exchange contributions from an unscreened interaction lead to all manner of disagreeable results. Screening is therefore necessary. But it is not sufficient, because were it not for the Pauli principle, the short-range interaction between the electrons would likewise lead to quite sizeable effects. It is perhaps gratifying that we conclude that the electron interactions do not alter the excitation spectrum appreciably, since it has been clear for some time that the simple extreme one-electron model is in good qualitative agreement with experiment.

The influence of exchange and correlation on various electron transport quantities cannot always be regarded as a simple state density correction. This question was first studied by Blatt (12) and recently [Barrie (13) has corrected certain aspects of Blatt's calculation. The electrical and thermal

conductivities of a metal involve the density of states at the top of the Fermi distribution and τ , the relaxation time for electron-phonon scattering. The energy level density is given by

$$(12) \quad \rho(E) = \frac{dn}{dE} = \frac{dn/dk}{dE/dk} = \frac{k^2}{\pi^2} \frac{1}{(dE/dk)}.$$

On the other hand, τ may be written as

$$(13) \quad \tau = \hbar^{-1} D k \left(\frac{dE}{dk} \right)^2$$

where D is a constant for a given metal. Both quantities are thus influenced by electron interaction through its influence on the first derivative of the one-electron energy, $E(k)$. On the other hand, the thermoelectric power of a metal involves also the second derivative, $\partial^2 E / \partial k^2$. The ratios of the actual electrical conductivity, σ , and thermoelectric power, S , to the values calculated in the free electron approximation, σ_0 and S_0 , may be written

$$(14a) \quad \sigma / \sigma_0 = (2A / X_1)^{-3},$$

$$(14b) \quad S / S_0 = A(X_1 + X_2) / X_1^2,$$

where $X_1 = [k(dE/dk)]_{E_0}$, $X_2 = [k^2(d^2E/dk^2)]_{E_0}$, and $A = (3.68/r_s^2)(m/m^*)$.

The effect of exchange and long-range electron correlations on the $E(k)$ curves may be simply calculated (see SSP, p. 407). It is rather more complicated to include the effect of the short-range electron correlations on $E(k)$. The reason lies in the fact that the expressions one obtains for $E(k)$ using standard perturbation-theoretic techniques to treat $H_{s,r}$, are lengthy and involved to evaluate. Recently, however, Fletcher and Larson (14) have carried this calculation out. Their results for the state density and the conductivity are given in Table IV and are in accord with one's expectation

TABLE IV

DENSITY OF STATES, CONDUCTIVITY, AND THERMOELECTRIC POWER OF THE ALKALI METALS: $\rho_0(E_0)$ IS THE FREE ELECTRON ENERGY LEVEL DENSITY AT THE TOP OF THE FERMİ DISTRIBUTION, $\rho_{\text{exch}}(E_0)$ THAT WITH THE INCLUSION OF EXCHANGE AND LONG-RANGE ELECTRON CORRELATIONS, AND $\rho_{\text{corr}}(E_0)$ THAT WITH THE INCLUSION OF SHORT-RANGE ELECTRON CORRELATIONS (AS WELL AS THOSE DUE TO EXCHANGE AND LONG-RANGE COULOMB INTERACTION), etc.

	Li	Na	K	Rb	Cs
r_s	3.22	3.96	4.87	5.18	5.57
m^*/m	1.45	0.98	0.93	0.89	0.83
k_c/k_0	0.63	0.70	0.78	0.80	0.83
$\rho_{\text{exch}}(E_0)/\rho_0(E_0)$	0.84	0.90	0.94	0.95	0.97
$\rho_{\text{corr}}(E_0)/\rho_0(E_0)$	1.14	1.11	1.18	1.19	1.18
$\sigma_{\text{corr}}/\sigma_0$	0.68	0.73	0.61	0.59	0.61
S_{exch}/S_0	0.81	0.91	0.99	1.01	1.05

that the effect of electron-electron correlations should be small. The correlations between electrons of antiparallel spin act to increase the state density, so that one finally finds for the alkali metals a state density slightly in excess of that found for free electrons. The influence of correlations on conductivity is considerably larger, and may be experimentally verifiable as calculations of D are improved.

Fletcher and Larson have also calculated the influence of short-range correlations on d^2E/dk^2 . They find that this expression becomes infinite at the Fermi surface. This divergence may be traced to the contributions to d^2E/dk^2 which arise from the interaction between electrons which lie on the Fermi surface. Such interactions lead to no difficulties with the expressions for $E(k)$ or dE/dk at the Fermi surface. Their influence on d^2E/dk^2 may be more satisfactorily taken into account by performing a more realistic calculation, in which the effect of temperature in spreading out the Fermi distribution is taken into account. It is expected that in such a calculation the divergence difficulties will disappear; whether these interactions will still have an important bearing on the expression for d^2E/dk^2 is not clear, and deserves careful investigation. I rather suspect that they will not, because if one cuts out a quite small fraction of the electron interactions, the subsequent expressions are well behaved and should lead to no startling results. For this reason I quote in Table IV S_{exch} , that is, S as influenced by exchange and long-range electron correlations.

In the foregoing we have neglected the influence of the subsidiary conditions on the one-electron energies, density of states, and the like. This is actually a rather good approximation. The electron energies are little affected by the subsidiary conditions because the readjustment of electron wave functions to obtain a wave function which satisfies the subsidiary condition involves only a slight amount of kinetic energy (2). One might still worry about the electronic specific heat, since some 15% of the degrees of freedom of the electron system appear to be inhibited by the subsidiary conditions. Actually, such an inhibition is of no practical importance. The subsidiary conditions may be shown to inhibit the degrees of freedom associated with an individual electron possessing an energy equal to the plasmon energy. (It is only at this point that there is a degeneracy between the plasmon system and the electron system, so that the possibility exists of there being too many degrees of freedom.) Such individual electron excitations are already completely frozen out by the Pauli principle, so that there is no need to invoke the subsidiary conditions in this regard.

IV. ACOUSTIC PLASMONS

I should now like to discuss the role that electron interaction may play in those solids in which there are two distinct groups of electrons. I have in mind electrons and holes in semiconductors, semimetals, and "s" and "d" electrons in the transition metals. We deal then with a "two-plasma" problem. If there were no interaction between the plasmas, we should expect to find plasmons of frequency Ω_p and ω_p , the heavy and light particle plasma frequencies respectively. Because of the interaction, the plasmon spectrum is altered, and it is the nature of this alteration and its implications for electron transport which I wish to discuss. The work which I am going to describe has been carried out in collaboration with Philippe Nozières. It is still in a very preliminary stage, as you shall see, so that what I have to say should perhaps be regarded as a somewhat premature progress report.

We may regard the existence of two kinds of charged particles as leading to two branches of the plasmon spectrum. In analogy to the phonon case, we may label these the optical branch and the acoustic branch. In the optical mode, the charged particles oscillate out of phase. The frequency is very nearly constant, and is given by

$$(15) \quad \omega_{\text{opt}} \cong \sqrt{(\omega_p^2 + \Omega_p^2)}.$$

In the acoustic mode, the particles oscillate in phase, with the light particles following the motion of the heavy particles. If one assumes that the acoustic plasmons are weakly coupled to either the light or heavy particles, their frequency is given by

$$(16) \quad \omega_s^2 = (k^2 \langle v^2 \rangle_{\text{AV}} / \omega_p^2) \Omega_p^2$$

where $\langle v^2 \rangle_{\text{AV}}$ is a suitable mean square velocity of the light particles. Because their frequency is low, these acoustic plasmons (or electronic sound waves) could conceivably play an important role in certain transport phenomena, and for this reason they bear closer investigation.

I shall here discuss only the circumstances under which acoustic plasmons might reasonably be expected to exist as an independent mode of elementary excitation of the electron system. Let us assume that

$$(17a) \quad \Omega_p^2 \ll \omega_p^2,$$

$$(17b) \quad \langle V^2 \rangle_{\text{AV}} \ll \langle v^2 \rangle_{\text{AV}},$$

where $\langle V^2 \rangle_{\text{AV}}$ is the heavy particle mean square velocity. These conditions turn out to be necessary conditions for the existence of an acoustic plasmon. Where they are satisfied, when the heavy particles move, the light particles will respond to their motion in such a way as to screen out the field of the heavy particles. We then have a situation closely analogous to that mentioned earlier for the electrons and ions in a metal. Again the heavy particle interaction is screened and as a result the natural vibrational frequency of the heavy particles is reduced from Ω_p^2 to $k^2 \lambda_c^2 \Omega_p^2$, where λ_c is the effective screening radius of the heavy particle interaction. It is this latter excitation of the heavy particles (screened by the light particles) which we call an electronic sound wave, or acoustic plasmon.

Nozières and I have carried out a Hamiltonian treatment of this problem, which is closely related to the electron-ion interaction treatment given in Reference 11. Here I wish only to sketch the results of our treatment. It is straightforward to show that where the effective particle interaction is given by

$$(18) \quad V(\mathbf{r}) = \sum_{\mathbf{k}} V_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}$$

the unperturbed plasmon frequency is given by

$$(19) \quad \omega_0^2 = N k^2 V_{\mathbf{k}} / M$$

when N , M are the density and mass of the particles under consideration. For the heavy particles interacting via the Coulomb interaction, we have

$$(20) \quad \omega_0^2 = \frac{Nk^2}{M} \frac{4\pi e^2}{k^2} = \Omega_p^2.$$

Now the light particles act to screen out the heavy particle interaction, so that V_k becomes

$$(21) \quad V_k \rightarrow V_k^{\text{eff}} \approx \frac{4\pi e^2}{k^2 + k_c^2} \approx \frac{k^2}{k_c^2} V_k = k^2 \lambda_c^2 V_k$$

for long wavelengths. We thus find, in the long wavelength limit,

$$(22a) \quad \omega_0 \sim Sk$$

where S , the acoustic plasmon velocity, is given by

$$(22b) \quad S = \lambda_c \Omega_p.$$

For a group of light particles obeying classical statistics, λ_c is simply the Debye length, $\lambda_d = \sqrt{(kT/4\pi n e^2)}$. In this case

$$(23) \quad S \sim S_{\text{class}} = \sqrt{\frac{kT}{M} \frac{N}{n}}$$

where N , n are heavy and light particle densities, respectively. If the light particles obey quantum statistics, λ_c is the Fermi-Thomas screening length,

$$\lambda_c = \lambda_{FT} = \frac{v_0}{\sqrt{3} \omega_p}$$

and

$$(24) \quad S \sim S_{\text{quantum}} = \frac{v_0}{\sqrt{3}} \frac{\Omega_p}{\omega_p}.$$

Thus far we have not placed any limits on the existence of the acoustic plasmons. They will, in fact, be coupled to both the light particles and the heavy particles and only when the coupling to both particles is weak will they exist as an independent mode of excitation. The coupling constant for the acoustic plasmon-light particle interaction turns out to be, approximately,

$$g^2 \cong S^2 / \langle v^2 \rangle_{\text{Av}}.$$

According to (16) and (17a) $g^2 \ll 1$, so that this coupling may always be neglected. The acoustic plasmon-heavy particle interaction coupling constant is

$$G^2 \cong k^2 \langle V^2 \rangle_{\text{Av}} / \omega_0^2 = \langle V^2 \rangle_{\text{Av}} / S^2$$

and the size of this coupling may frequently prove the determining factor in the existence of acoustic plasmons. Where $G^2 \ll 1$, the acoustic plasmons describe well the long wavelength motion of the heavy particles, and the damping of an acoustic plasmon by the heavy particles is negligible.

To sum up, we find that acoustic plasmons constitute an independent mode of elementary excitation of the "two-plasma" system when

$$(25) \quad \langle V^2 \rangle_{\text{Av}} \ll S^2 \ll \langle v^2 \rangle_{\text{Av}}.$$

This requirement includes the conditions (17a), (17b), since $S^2 \ll \langle v^2 \rangle_{\text{Av}}$

implies (17a). It goes beyond these conditions, in that we must also have $\langle V^2 \rangle_{AV} \ll S^2$. Where these conditions are satisfied the acoustic plasmon is a sound wave with an approximately constant velocity which lies between the average light particle and heavy particle velocities, and we should expect that the presence of acoustic phonons would influence the transport properties of the solid. The cases in which the foregoing criteria may be satisfied are now under investigation. Let me conclude by listing some unlikely and likely prospects for acoustic plasmons. Amongst the unlikely prospects should be mentioned:

1. Two groups of classical electrons of the same density at the same temperature. ($\langle V^2 \rangle_{AV} \ll S^2$ cannot be satisfied.)

2. A degenerate gas of two kinds of holes in heavily doped "p" type Ge. ($S^2 \ll \langle v^2 \rangle_{AV}$ is not compatible with $\langle V^2 \rangle_{AV} \ll S^2$.)

The likely prospects include:

1. Classical gases of electrons and holes of different masses and concentrations in semiconductors.

2. Semimetals with two quite different groups of electrons.

3. Classical holes and electrons at different temperatures.

Whether the acoustic plasmons can be produced, or detected via their scattering properties, then becomes a matter for detailed investigation for the material one has in mind.

In conclusion, I might say that the possibilities in semiconductors are sufficiently varied for it to be possible to establish the existence, under suitable circumstances, of acoustic plasmons in these materials. If they are found, it might be good to have a separate name for this type of elementary excitation, "acoustic plasmon" being a bit awkward. Now such excitations may occur in a classical electron system. I have always thought it too bad that Maxwell lived too early to have a particle or excitation named in his honor. Therefore I suggest that in honor of Maxwell, and because we deal here with a case of distinct electron motion (or D.E.M.), we call these new excitations, "demons".

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DISCUSSION OF PINES'S PAPER

Fröhlich: The velocity of a demon in the classical case is identical with the velocity of sound in a gas.

Pines: Yes.

Price: Could you not treat a liquid metal as a system of light particles (electrons) and heavy particles (nuclei) in much the same way as you have considered light and heavy carriers in solids?

Pines: At very high temperatures where periodic effects no longer persist this might be all right. But with strong short-range interactions the treatment is very difficult; for example, consider the somewhat analogous case of liquid helium.

Aigrain: You said that demons should not exist in *p*-type germanium. But they might exist if you made the light particles hot, by means of a strong electric field.

Bardeen: The same applies to a gas plasma in which two sets of particles are at different temperatures.

Bhatia: How important are cross-terms between phonons and plasma?

Pines: The coupling constant is about 10^{-6} .

Joffé: Consider semiconductors, most of which have a very low electron mobility. The mean free path is estimated to be about 0.1 \AA —much less than the wavelength of the electrons. Typically the velocity of an electron in a semiconductor is about $10^7 \text{ cm. sec.}^{-1}$; while the uncertainty in velocity deduced from the Heisenberg principle is \AA hundred times greater. Clearly the conventional mode of description is not adequate, and the whole theory of transport phenomena in these substances needs radical revision.

Pines: The problem you mention is indeed a difficult one, quite apart from its collective aspects. With regard to the latter, however, I might say that, though the mean free path of one of the charged particles may be very short, one might still get a demon, since the demon represents a polarization wave in the solid. It is not out of the question that we might observe a moving polarization wave even when the particles which give rise to it are essentially bound at the various lattice sites.

Chambers: I should like to ask a naive question which I think is just the old question about the subsidiary conditions. You start with N electrons

having $3N$ degrees of freedom: you end with N screened electrons having $3N$ degrees of freedom, together with an extra N' degrees of freedom due to the plasma modes. Is there any logical way out of this difficulty?

Pines: If we introduce N' plasma degrees of freedom, we have of course N' subsidiary conditions. This takes care of the *logical* difficulty. In *practice*, neglect of the subsidiary conditions doesn't affect the energy or specific heat much; but the wave function is appalling.

To be more specific on this latter point, let me say that we expect to get into trouble with the specific heat when we get a one-electron excitation of the order of the plasmon energy. But the Pauli principle has already effectively frozen out such a high energy excitation, so that the difficulty doesn't arise. We expect of course an effect in the classical case.

Seeger: Would you like to say something about s - d correlation in copper?

Pines: For copper the plasma formed from s electrons has an energy quantum of about 11 ev. Its interaction with d electrons causes a shift to about 20 ev. The perturbation approach is therefore not at all good, and we need something better which as yet we have not developed. I might add that I believe that we need a proper treatment of s - d coupling before we can expect to get a proper theory of ferromagnetism.

Price: Presumably the mean free path of a demon tends to be long (as you report) because it depends on a deformation potential which is the change of forbidden *gap* with strain.

Of course, for heat transport by demons one would not observe a line spectrum of recombination radiation at the cold end of the crystal (cf. discussion of Joffé's paper).

Friedel: In his analysis of 'demons', Pines considers only the correlation between heavy and light particles, not the direct correlation between heavy particles. This seems to me possible only if light particles have a screening radius smaller than heavy particles. For fermions and using first-order approximations, the condition is for light particles to have a density of states at the Fermi level larger than that of the heavy ones (Friedel, *Advances in Physics*, **3**, 466 (1954)). This condition is *not* fulfilled, as regards conduction electrons and d holes, in any of the usual transitional metals and alloys, except perhaps in alloys such as Ni 50%, Cu 50% with an almost full d band, where it might possibly be related to the anomaly in low temperature specific heat (W. H. Keesom and B. Kurrelmeyer, *Physica*, **7**, 1003 (1940)). The magnetic behavior of ferromagnetic alloys may be taken as an experimental proof that the condition on screening stated above is usually not fulfilled: when say cobalt or copper is substituted in nickel, the change in nuclear charge is screened out by a local displacement of d holes, giving to the impurity a magnetic moment different from that of the matrix, and not by a repulsion of s electrons, which would not alter its magnetic moment (Friedel 1954, *loc. cit.*).

OUR KNOWLEDGE OF THE FERMI SURFACE¹

By R. G. CHAMBERS²

INTRODUCTION

If we accept the one-electron model of a metal as a working approximation, it is clear that for an understanding of the properties of any given metal the first requirement is a knowledge of the shape of the energy surfaces $E(\mathbf{k})$ in wave-number space (\mathbf{k} -space), particularly in the region of the Fermi energy E_0 , and the second is a knowledge of the relaxation time $\tau(\mathbf{k})$ (or, if a unique relaxation time does not exist, some other suitably defined collision parameter), preferably over a wide temperature range. Even if the one-electron model is abandoned, it seems probable that any more refined model, if it is to be at all tractable, will involve similar parameters, and methods of determining such parameters are therefore of considerable interest.

It is of course possible to calculate $E(\mathbf{k})$ purely theoretically, by solution of the Schrödinger equation for an electron moving in a periodic potential, and this approach has been vigorously developed in the past ten years, particularly by Professor Slater's group at M.I.T., but the results obtained so far are usually at best semiquantitative because of uncertainties in the precise form of the periodic potential and other quantities involved. Calculations of this sort can, however, give valuable guidance in the interpretation of experimental results, and a combination of the two approaches, theoretical and experimental, may suffice to determine the shape of the Fermi surface almost completely, as we shall see later.

Very few attempts have yet been made to calculate $\tau(\mathbf{k})$ theoretically, except for free electrons, and if one takes into account the detailed form of the lattice vibration spectrum as well as the detailed shape of the Fermi surface, the problem is indeed of forbidding complexity. It may be simpler, however, to calculate the scattering by static imperfections, and this would be of particular interest for comparison with experiment, because the experimental methods at present available are limited in application to very low temperatures, where scattering by static imperfections greatly outweighs thermal scattering. It is unfortunate that at present neither theory nor experiment can give us any detailed information about thermal scattering.

I shall not attempt to review here the progress which has been made in the purely theoretical calculation of $E(\mathbf{k})$, which is outside my province; I shall confine myself instead to a discussion of the methods available for attacking the problem experimentally, and the results which have been obtained.

MAGNETORESISTANCE

Most of the more simply measurable properties of metals are either scalars or simple tensors, and it is obvious that these cannot contain enough informa-

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tion to determine the shape of the whole Fermi surface. Much more experimental information can be accumulated by measuring the transport properties of single crystals in a magnetic field, and here Shockley (1950) has shown how the conductivity tensor may be evaluated theoretically in terms of $E(\mathbf{k})$ and $\tau(\mathbf{k})$ for any magnetic field strength, if it is assumed that the Boltzmann equation and the Lorentz force equation are applicable and that $\tau(\mathbf{k})$ exists. If these assumptions are accepted, measurements of the complete conductivity tensor as a function of field strength probably contain, in principle, all the information needed for the evaluation of $E(\mathbf{k})$ and $\tau(\mathbf{k})$, but in such complex form that there seems little hope of evaluating them directly from such measurements, in the general case. If it can be assumed, however, that the $E(\mathbf{k})$ surfaces are ellipsoids and that τ depends only on energy, theoretical evaluation of the conductivity tensor is greatly simplified, and many workers have considered models of this type. In particular, such models can reproduce quite closely the observed conductivity tensors of germanium (Abeles and Meiboom 1954; Shibuya 1954), silicon (Pearson and Herring 1954), and bismuth (Abeles and Meiboom 1956), and moreover the ellipsoidal energy surfaces thus found agree well with those deduced by other methods. It is to be expected theoretically that some at least of the energy surfaces in these materials should be ellipsoidal, and Herring (1955) has given theoretical reasons for expecting that for such surfaces a relaxation time should exist and that it should depend only on energy. These materials are thus particularly suitable for study in this way, and magnetoresistance studies are likely to be of less value in metals with more complex $E(\mathbf{k})$ and $\tau(\mathbf{k})$ surfaces, except possibly as a check on information obtained in other ways.

For general $E(\mathbf{k})$ and $\tau(\mathbf{k})$, it is not difficult to deduce expressions for the conductivity tensor in the limit of very high magnetic fields, where $\omega_c \tau \gg 1$, ω_c being the cyclotron frequency of the electrons; in particular, it can be shown that in the presence of a field H_z , the conductivity component σ_{xx} should vary as H^{-2} if the Fermi surface defines a number of separate simply connected regions, but that it may contain a term independent of H if the Fermi surface is multiply connected. It has been suggested by Lifshitz, Azbel', and Kaganov (1956) that such measurements might therefore enable one to distinguish between these two possibilities, and so obtain useful qualitative information about the Fermi surface. Unfortunately it is found experimentally (Chambers 1956a) that for Cu, Ag, and Au σ_{xx} varies in neither of these ways at high fields, but as $|H|^{-1}$. This behavior is at present unexplained: it is possibly due to field-dependent scattering of electrons by dislocations, but until it is elucidated, such measurements clearly cannot be used to obtain even qualitative information about the Fermi surface.

The difficulty of interpreting magnetoresistance measurements theoretically arises because the theoretical expression involves a complicated average over both $E(\mathbf{k})$ and $\tau(\mathbf{k})$. There are three phenomena for which the problem of interpretation is very much simpler, because they depend primarily on rather simple averages over the energy surfaces, which involve the relaxation time only slightly, if at all. We shall discuss these phenomena—cyclotron resonance, the anomalous skin effect, and the de Haas – van Alphen effect—in turn.

CYCLOTRON RESONANCE

The remarkable success of cyclotron resonance experiments in elucidating the structure of germanium and silicon is well known (see, e.g., Dresselhaus, Kip, and Kittel 1955), and we need not review this work here. It is natural however to ask how far similar techniques can be applied to other materials, and for this purpose we first summarize briefly the conditions for cyclotron resonance. Following Shockley (1950, 1953), we assume that the motion of a wave-packet in \mathbf{k} -space is given by the Lorentz equation

$$(1) \quad \hbar \dot{\mathbf{k}} = e(\mathbf{v} \times \mathbf{H})/c$$

where $\mathbf{v} = \hbar^{-1} dE/d\mathbf{k}$. Thus in the presence of a field H_z , k_z remains constant and the electron moves around an orbit in \mathbf{k} -space formed by the intersection of a constant-energy surface with the plane $k_z = \text{constant}$. If we set up curvilinear coordinates k_t and k_n in this plane such that k_t is measured along the orbit and k_n normal to it, we have

$$\hbar dk_t/dt = (eH_z/\hbar c) dE/dk_n,$$

i.e.

$$dt = (\hbar^2 c/eH_z) (dk_n/dE) dk_t,$$

so that if the orbit is closed, the periodic time τ_c is given by

$$(2) \quad \tau_c = (\hbar^2 c/eH_z) \oint (dk_n/dE) dk_t = (\hbar^2 c/eH_z) d\mathcal{A}/dE$$

where \mathcal{A} is the area enclosed by the orbit in the plane $k_z = \text{constant}$, and the corresponding cyclotron frequency is given by

$$(3) \quad \omega_c = 2\pi/\tau_c = (eH_z/c) (2\pi/\hbar^2) dE/d\mathcal{A} = eH_z/m^*c$$

where the 'orbit mass' m^* is given by

$$(4) \quad m^* = (\hbar^2/2\pi) d\mathcal{A}/dE.$$

If now the mean relaxation rate $(1/\tau)$ around the orbit is small so that $\omega_c \gg (1/\tau)$, and we apply a spatially uniform field of frequency ω , circularly polarized in the x - y plane, resonance absorption of energy will occur when $\omega = \omega_c$, and from observation of the resonance m^* and $d\mathcal{A}/dE$ can be deduced.

Germanium and silicon are again particularly favorable materials for study by cyclotron resonance techniques, first because the carrier concentration in pure material is so low that an r-f. electric field will penetrate it almost uniformly, and secondly—as in magnetoresistance studies—because the energy surfaces for the conduction electrons are ellipsoidal, and depend quadratically on k . In this case the value of m^* for a given ellipsoid is the same for all values of (E, k_z) , i.e. for all orbits, so that all electrons in that ellipsoid resonate at the same frequency, and so a single well-defined line is obtained from each ellipsoid. If $\omega_c \gg (1/\tau)$, equation (3) at once gives m^* (which of course varies with the direction of magnetic field relative to the ellipsoid), and the line width gives an average of $(1/\tau)$ over all orbits. If ω_c is not large compared with $(1/\tau)$, the resonance peak may be displaced somewhat from $\omega = \omega_c$, but from the line shape it is still possible to deduce both ω_c and τ , if τ can be assumed to be constant over the ellipsoid.

The situation in the valence band of Ge and Si is much less straightforward, and more representative of what might be expected in ordinary metals: the

energy surfaces now form not simple ellipsoids but 'fluted spheres', and m^* is no longer constant over the surface. The resonance lines are thus now inherently broadened by the spread in values of ω_c , as well as by collisions, and the problem of exact interpretation becomes rather formidable. If it is assumed that the position of the resonance peak is determined by the extremal value of m^* , and that this occurs at $k_z = 0$, the problem is considerably simplified, and in this way Dexter *et al.* (1954) and Dresselhaus *et al.* (1955) have succeeded in fitting the observed variation of ω_c with orientation to a theoretically predicted model; they have also shown that the error involved in the use of this approximation should be small. As we shall see later, it should be possible to deduce useful information about the energy surfaces directly from a knowledge of the extremal m^* as a function of orientation, even when a theoretical model is not available as a basis for analysis. The fact that cyclotron resonance experiments yield a mean value of m^* , rather than the extreme value, may however make analysis difficult in unfavorable cases.

As remarked above, cyclotron resonance experiments are particularly straightforward with Ge and Si, because of the low carrier concentration: in metals, an r-f. electric field applied normal to the surface is completely screened out by the conduction electrons, and an r-f. field applied parallel to the surface penetrates only to a small depth because of the skin effect. If the metal behaves classically, in the sense that the current density at any point is related simply to the electric field at that point, the result of the skin effect will be to change the resonance from an absorption peak to an absorption edge (Anderson 1955), but it should still be possible to interpret the results in terms of values of m^* . In fact, however, if the conditions are chosen so that $\omega\tau \gg 1$ (as required for cyclotron resonance), any normal metal will be in the extreme anomalous skin effect region, where the skin depth is small compared with the mean free path of the electrons and a point relation between current and electric field no longer exists. This greatly complicates the theoretical analysis. If the magnetic field is applied normal to the surface of the metal, it is easy to show that the resonance is almost completely suppressed (Azbel' and Kaganov 1954; Chambers 1956b), and this accounts for the failure to observe it experimentally under these conditions. Bismuth appears to be a border-line case, in which the skin effect conditions in a magnetic field are not sufficiently anomalous to suppress the resonance completely: Galt *et al.* (1955) and Dexter and Lax (1955) have found several resonances, and Lax *et al.* (1956) have attempted to explain these in terms of a classical skin-effect theory. It appears, however, that for normal metals it would be necessary to work at infrared frequencies, and at fields of order 500 kilogauss (kG.) or more, to obtain useful results with this geometry.

It has recently been pointed out, however, by Azbel' and Kaner (1956) that if the magnetic field is applied parallel to the surface of the metal, cyclotron resonance should be much more readily observable. A detailed theoretical treatment of this geometry is exceedingly difficult, even for a free-electron metal (cf. Azbel' 1955), but it is easy to show qualitatively how the resonance comes about. A free electron in a magnetic field will pursue a helical path

in real space, and an electron in a lattice, moving in a closed orbit in \mathbf{k} -space, will pursue a qualitatively similar path, whose projection normal to the magnetic field is the same in shape as the orbit in \mathbf{k} -space, but rotated through 90° . Thus if, as in Fig. 1, the magnetic field is applied parallel to the surface

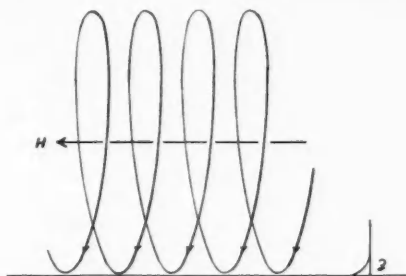


FIG. 1. Illustrating the possibility of cyclotron resonance in metals (Azbel' and Kaner 1956).

of the metal, an electron which approaches close to the surface at one point in its path will again do so at time intervals $\tau_c = 2\pi/\omega_c$ until it suffers a collision. If now an electric field of frequency ω is applied at the surface, its penetration depth will for normal metals be much less than the radius of the orbit, as shown, so that the electron will suffer an impulsive acceleration at intervals τ_c ; if $\omega = \omega_c$, successive impulses will be in phase, and if $\omega_c \gg (1/\tau)$, a resonance will occur. Moreover resonance will again occur whenever $x = \omega/\omega_c$ is integral: the electric field then undergoes x oscillations while the electron completes one cycle. According to Azbel' and Kaner, the resultant effect is, approximately, to modulate the surface impedance of the metal by a factor

$$[1 - \exp(-2\pi ix) \exp(-2\pi x/\omega\tau)]^{\frac{1}{2}}$$

where τ is written for $(1/\tau)^{-1}$. Thus the impedance varies approximately sinusoidally with x (i.e. with $1/H$); the effect of increasing $\omega\tau$ is not to sharpen the resonance but merely to increase the number of oscillations observable.

It seems probable that just this effect has been observed by Fawcett (1956) in experiments on the surface resistance of tin at 24,000 Mc./sec. Fig. 2 shows one of his curves, in which the ratio R/R_0 of surface resistance to its zero-field value is plotted against field strength; for this specimen at this frequency he estimates $\omega\tau \sim 27$. The upper curve shows the behavior predicted by Azbel' and Kaner for a spherical or ellipsoidal Fermi surface with $\omega\tau = 10$, plotted against H/H_0 where $H_0 = m^*c\omega/e$. The curve is drawn here taking $H_0 = 2$ kG., which gives $m^* \sim 0.24m$, a not implausible value. Fawcett has found that if the tin is alloyed with indium to reduce τ , the 'resonance' disappears, as expected. The rapid initial fall in R/R_0 found experimentally is not predicted by Azbel' and Kaner, but their paper gives only a preliminary survey of the effect, and a complete theory may well show such behavior, even for a free-electron model. Only the fundamental resonance $\omega = \omega_c$ appears to be observed

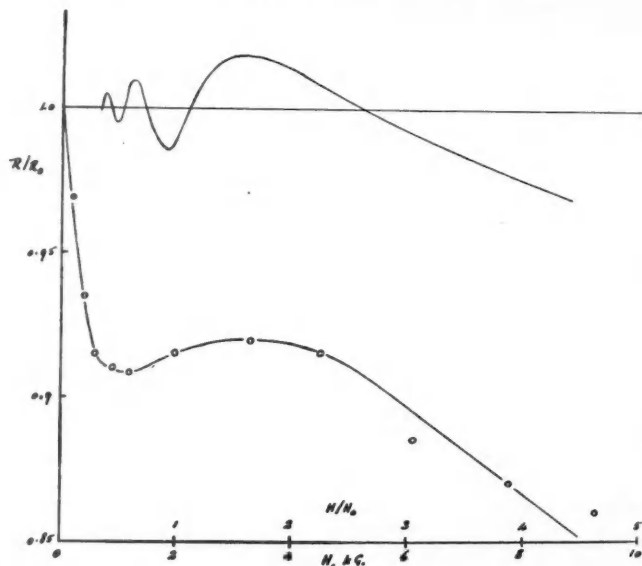


FIG. 2. Cyclotron resonance: comparison of Azbel' and Kaner's theoretical curve (above) and Fawcett's experimental results on tin (below).

experimentally, and this might be expected if there is any spread in the values of m^* over the Fermi surface. Such a spread will result in a blurring of the resonance, which increases progressively for the higher harmonics: if the range of values of m^* exceeds about 1:1.5, all but the fundamental are practically obliterated.

Azbel' and Kaner suggest that the resonance condition is determined simply by the extremal value of m^* ; this is the approximation also made by Dexter *et al.* and by Dresselhaus *et al.* We have already remarked that this approximation may not always be adequate, and that the value of cyclotron resonance experiments would be considerably increased if they could be made to yield the value of m^* for some definite value of k_z , rather than an average value. With the present type of experiment this may be possible. Azbel' and Kaner have pointed out that if the magnetic field is not exactly parallel to the surface, the resonance will be largely suppressed—referring to Fig. 1, it is clear that the path of the electron will then pass only once through the surface layer, so that it will not contribute to the resonance—and they estimate that for resonance to occur, the angle between field and surface must be less than $(\delta/r)^{2/3}$, where δ is the skin depth and r is the radius of the orbit; i.e. less than about 1° . But there is clearly one group of electrons for which resonance will not be suppressed, consisting of those which pursue closed orbits in real space rather than helical orbits, i.e. those for which the average velocity v_z in the direction of the field is zero or very small: these will return to the same place in the surface layer after each orbit, even if the field is tilted. It thus seems

probable that if a resonance can still be observed when the field is deliberately set at a slight angle to the surface, it will yield the value of m^* for just this localized group of electrons, rather than an average over the whole Fermi surface, and if so the interpretation of the results will be considerably easier.

At present too little is known about this form of cyclotron resonance to assess its value as a tool in the study of energy surfaces: it appears to be very promising, but with many metals, it may be difficult to attain the condition $\omega\tau \gg 1$, and even when this condition is attained, the width of the resonance may limit rather severely the accuracy of the results.

THE ANOMALOUS SKIN EFFECT

The possibility of using anomalous skin effect measurements to study the energy surfaces of metals has been reviewed by Pippard (1955); here we shall outline the basic physical ideas of his treatment, discuss some necessary modifications to them, and review the experimental data so far available.

We recall that the surface resistance R is defined as the real part of the surface impedance Z , which is the ratio of the r.f. electric field $\mathcal{E}(0)$ at the surface ($z = 0$) to the total current flowing, $\int_0^\infty J(z)dz$. Using Maxwell's equations, and neglecting the displacement current (as is permissible here), we can write Z (in e.m.u.) in the alternative forms:

$$(5) \quad Z = R + iX = \mathcal{E}(0)/\int_0^\infty J(z)dz = 4\pi\mathcal{E}(0)/H(0) = -4\pi i\omega\mathcal{E}(0)/(d\mathcal{E}/dz)_0.$$

Maxwell's equations also yield the relation

$$(6) \quad d^2\mathcal{E}/dz^2 = 4\pi i\omega J;$$

if Ohm's law holds, combination of (6) with $J = \sigma\mathcal{E}$ at once yields the classical skin effect equations for $\mathcal{E}(z)$, for the skin depth δ_0 , and for Z :

$$(7) \quad \mathcal{E}(z) = \mathcal{E}(0)\exp[-(1+i)z/\delta_0], \quad \delta_0 = (2\pi\omega\sigma)^{-1/2}, \quad Z = (4\pi i\omega/\sigma)^{1/2}.$$

Thus at a given frequency, $\Sigma \equiv 1/R$ should increase uniformly with $\sigma^{1/2}$. It was first noticed by London (1940) that for tin at 1000 Mc./sec. and 4° K. Σ was much smaller than the value predicted by (7), and he suggested that this was because under these conditions the electronic mean free path was about a thousand times greater than the value of δ_0 predicted by (7), so that the electron no longer moved in a constant field between collisions. Ohm's law then breaks down, and must be replaced by an integral relation between J and \mathcal{E} , and when this is combined with (6) we obtain an integrodifferential equation for $\mathcal{E}(z)$. This equation, for free electrons, was set up and studied by Pippard (1947) and solved by Reuter and Sondheimer (1948) in the limiting cases of diffuse reflection, where the electrons lose their drift momentum on collision with the surface ($p = 0$), and specular reflection, in which drift momentum is retained ($p = 1$). They found that the behavior of Σ was very similar in the two cases, and that in the limit $\delta_0 \ll l$, Σ tended to a constant value Σ_∞ , varying as $\omega^{2/3}$ and independent of σ . Just such behavior was found experimentally (Pippard 1947), and it has also been found experimentally that the variation of Σ with σ follows closely the theoretical curve for $p = 0$, i.e. for diffuse reflection at the surface (Chambers 1952).

The quantity of interest to us here is the surface conductance Σ_∞ in the extreme anomalous limit. (The use of the word anomalous in this way is perhaps reprehensible, but convenient.) For free electrons, Pippard (1947) gave a simple physical argument—the 'ineffectiveness concept'—to explain the existence of a limiting value for Σ , and it was by an extension of the same argument that he later obtained an expression relating Σ_∞ to the geometry of the Fermi surface in the general case (Pippard 1954). The argument is based on the fact that in the anomalous limit, the theoretically calculated value of $\int_0^\infty \mathcal{E} dz$ becomes very small. It is therefore supposed that electrons which travel without collision from the interior of the metal to the surface contribute very little to the total current; the only ones which contribute significantly are those which have an appreciable probability of collision within the skin depth δ (which has yet to be determined), i.e. those travelling almost parallel to the surface of the metal, which spend an appreciable fraction of their mean free path within the skin depth. Thus if we assume that the only electrons effective are those travelling at angles less than $\beta\delta/l$ to the surface, where β is an adjustable parameter, and furthermore that for these electrons $J(z)$ can be evaluated as if they moved in the constant field $\mathcal{E}(z)$, then $J(z)$ and $\mathcal{E}(z)$ are related simply by an effective conductivity σ_{eff} , and for free electrons it is found that $\sigma_{\text{eff}} = \frac{2}{3}\beta\delta\sigma/l$, where σ is the d.c. conductivity. Inserting $J = \sigma_{\text{eff}}\mathcal{E}$ in (6), we now obtain

$$(8) \quad \begin{aligned} \mathcal{E}(z) &= \mathcal{E}(0) \exp[-(1+i)z/\delta], & \delta &= (2\pi\omega\sigma_{\text{eff}})^{-\frac{1}{2}} = (3\pi\omega\beta\sigma/l)^{-\frac{1}{2}}, \\ Z &= -4\pi i\omega \mathcal{E}(0)/(d\mathcal{E}/dz)_0 = (1+i)2\pi\omega\delta = (1+i)(8\pi^2\omega^2 l/3\beta\sigma)^{\frac{1}{2}}. \end{aligned}$$

Now σ/l is a constant parameter independent of σ , so that (8) does indeed lead to a surface impedance independent of σ , as found experimentally in the extreme anomalous limit, and as found also by Reuter and Sondheimer in their exact analysis: quantitative agreement with their values of R is obtained if we choose $\beta = 4.84$ for $p = 0$ and 6.89 for $p = 1$. The exact analysis however gives $X = \sqrt{3}R$, as do the experiments, whereas this approximation gives $X = R$. It is a fairly straightforward matter to generalize the ineffectiveness concept approach to the problem of an arbitrary Fermi surface, and Pippard's (1954) analysis of this case forms the basis for interpreting anomalous skin effect measurements on single crystals in terms of the Fermi surface geometry. Clearly such an extension of the treatment required some justification before any confidence could be placed in it, and this was provided by a comparison with the exact treatment by Sondheimer (1954) of the problem for spheroidal energy surfaces: it turned out that the two treatments yielded identical expressions for R , if the same values of β were chosen as for the free-electron problem.

The ineffectiveness concept treatment thus depends on two points: the fact that $\int_0^\infty \mathcal{E} dz$ becomes very small in the extreme anomalous region, and the consequent assumption that the total current $\int_0^\infty J dz$ is carried only by electrons travelling at glancing angles to the surface. It is a little disturbing to find, therefore, that for $p = 1$ these two quantities are quite generally related, for any Fermi surface, simply by

$$(9) \quad \int_0^\infty J dz = \sigma \int_0^\infty \mathcal{E} dz$$

where σ is the ordinary d-c. conductivity tensor, and that the proportion of the total current carried by any given group of electrons is precisely the same as under d-c. conditions. This result, which is easily obtained from the Reuter-Sondheimer equations, holds under all conditions from the classical to the extreme anomalous limit. For $p = 0$ the result is slightly modified: in the classical limit (9) again holds, but in the anomalous limit σ must be replaced by $\sigma/2$; again, the effectiveness of any group of electrons is essentially the same as under d-c. conditions. Fortunately, Pippard's results for a general Fermi surface have since been derived by Kaganov and Azbel' (1955) by a more rigorous argument not involving the ineffectiveness concept, and an examination of their treatment shows that the ineffectiveness concept, though not generally valid, is in fact valid for extremely small z ($\ll \delta$): in this region $J(z)$ is carried only by small-angle electrons, and moreover $J(z) \propto \mathcal{E}(z)$, so that the field falls off exponentially: $\mathcal{E}(z) \sim e^{-az}$. The field rapidly ceases to obey an exponential law at greater distances, but from (5) it is clear that Z is determined by its behavior in the immediate neighborhood of the surface; thus even though the ineffectiveness concept is only valid within this region, this suffices to determine Z correctly. Moreover, if $\mathcal{E}(z) \sim e^{-az}$ in this region, and we write $J = \beta b \mathcal{E}/a$, where b has the dimensions of (σ/l) and β has the same value as before, we have from (6)

$$a^2 = 4\pi i \omega \beta b / a,$$

and so from (5),

$$(10) \quad Z_\infty = 4\pi i \omega / a = (4\pi i \omega)^{2/3} (\beta b)^{-1/3} = \frac{1}{2} (1 + \sqrt{3}i) (4\pi \omega)^{2/3} (\beta b)^{-1/3},$$

which thus gives the correct ratio X/R .

According to both Pippard and Kaganov and Azbel', the quantity b , and hence Z , can be expressed in terms of the geometry of those parts of the Fermi surface where the normal to the Fermi surface is parallel to the surface of the metal: i.e. the regions associated with small-angle electrons. In fact if the direction of the normal at any point on the Fermi surface is specified with respect to the z axis by polar coordinates (θ, ϕ) , and $K(\theta, \phi)$ is the Gaussian curvature of the Fermi surface in \mathbf{k} -space at that point, then

$$(11) \quad b = (e^2/4\pi^3\hbar) \int_0^{2\pi} \cos^2 \phi d\phi / K(\frac{1}{2}\pi, \phi);$$

this value of b , inserted in (10), gives the value of Z ($=Z_x$ say) when the electric field is directed along $\phi = 0$. For this to be true, we must choose the origin of ϕ so that

$$(12) \quad \int_0^{2\pi} \sin \phi \cos \phi d\phi / K(\frac{1}{2}\pi, \phi) = 0;$$

then (11) and the similar expression with $\cos^2 \phi$ replaced by $\sin^2 \phi$ give Z_x and Z_y , and values of Z for intermediate directions follow at once by superposition.

The condition (12) is necessary in order that the coupled set of integro-differential equations which governs the problem shall be separable into independent equations in \mathcal{E}_x and \mathcal{E}_y ; for the same reason Kaganov and Azbel' found it necessary to make one approximation in their analysis (also made by Sondheimer in treating the spheroidal model)—that \mathcal{E}_z could be neglected. It is easy to see from the form of their equations that the effect of \mathcal{E}_z will be small for small-angle electrons; it follows from (9) that the effect will also in general be small for large-angle electrons, since $\int_0^\infty \mathcal{E}_z dz$ will in general be small; some error may however be introduced by this approximation for metals with a highly anisotropic d-c. conductivity tensor.

Apart from this, their analysis is exact, and it follows that Z_∞ is determined by the properties of a very localized region of the Fermi surface, and is quite independent of the relaxation time (Azbel' and Kaner (1955) have shown that this remains true if $\tau(\mathbf{k})$ is replaced by an arbitrary collision operator, and also, apart from a numerical factor of order unity, if p is replaced by an arbitrary surface collision operator). Thus from measurements of Z_∞ for a range of crystal orientations, one may hope to be able to deduce the Gaussian curvature K at all points on the Fermi surface, and thus derive the detailed shape of the surface. As pointed out by Pippard, ambiguities may arise if the Fermi surface is not a single convex surface, because more than one point on the surface may then be specified by given (θ, ϕ) , and the measurements will then yield the reciprocal sum of the Gaussian curvatures over all such equivalent points; consideration of zone structure and of other experimental information may help to resolve such ambiguities.

Experimentally, to obtain useful results it is necessary to work at a high microwave frequency and to use metal of the highest possible purity, just as in cyclotron resonance experiments: there we needed $\omega\tau \gg 1$; here we need $l \gtrsim 10^7 \delta_0$ if Z is not to differ appreciably from Z_∞ . The latter condition is usually somewhat the less restrictive, but it is sufficient to preclude the study of alloys, for instance. Moreover, since $b \propto Z_\infty^{-3}$, it is necessary to measure Z_∞ with rather high accuracy; a difficulty here is that Z_∞ is particularly sensitive to surface imperfections, and it is essential to use electrolytically polished specimens, free from surface strains and free from surface roughness on a scale comparable with δ .

Fawcett (1955) has carried out a careful investigation of tin in which these conditions were fulfilled, and has found a wide range of variation of $\Sigma_\infty = 1/R_\infty$ with orientation, as shown in Fig. 3. Here θ, ϕ have a different significance from that used above: θ is the angle between the tetrad axis and the normal to the surface of the metal, and ϕ the azimuth angle of the dyad axis about the tetrad axis; for $\phi = 0$, the dyad axis is parallel to the surface of the metal. The dashed curves show the values of Σ_∞ calculated theoretically by Fawcett, using (10), (11), for a model of the Fermi surface consisting of three ellipsoids: the fit is good enough to suggest that his model may represent quite closely the true Fermi surface, but he was unable to reconcile it with the zone structure of tin given by Mott and Jones (1936). Examination shows, however, that the structure proposed by them is incorrect: though the [110] planes have zero

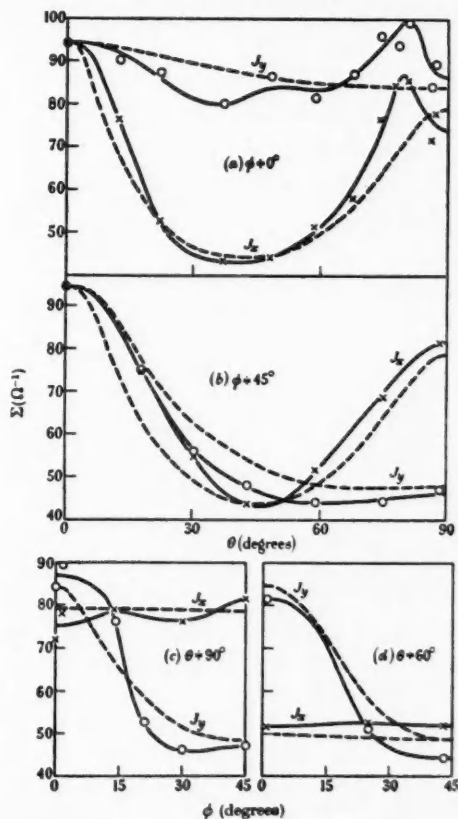


FIG. 3. Anomalous skin effect: variation of surface conductance of single crystals of tin with orientation (Fawcett 1955). — — —, ellipsoidal model of the Fermi surface.

structure factor, energy discontinuities are generated across them by the combined action of the potentials V_{101} and V_{211} (in the notation of Mott and Jones; quite generally, if $V_{\mathbf{a}}$ and $V_{\mathbf{b}}$ are non-zero, so that \mathbf{a} and \mathbf{b} define planes of energy discontinuity, then $\mathbf{a}-\mathbf{b}$ will also be a plane of energy discontinuity, even if $V_{\mathbf{a}-\mathbf{b}} = 0$). The reduced zone is in fact formed by the planes $[110]$ and $[101]$; this zone, which contains two electrons per atom, is shown in Fig. 4, which also shows the ellipsoids of Fawcett's model. The dimensions marked are in units of 10^8 cm^{-1} . It will be seen that two of his ellipsoids fit very comfortably onto the $[110]$ faces of the zone; the remaining one, however, which in his model is an ellipsoid of revolution about the tetrad axis, clearly cannot be accommodated as it stands. A more plausible model might consist of four smaller ellipsoids fitted onto the $[101]$ faces, and the resultant tilted ellipsoids might well account for the maximum in Σ_{∞} found by Fawcett at

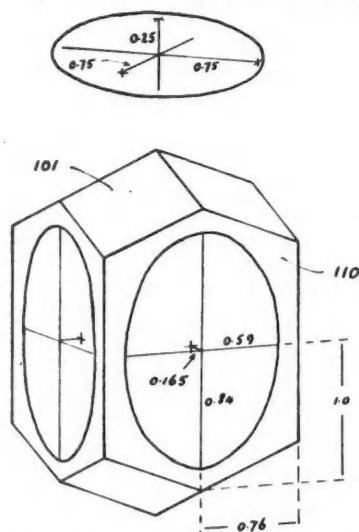


FIG. 4. Zone structure of tin, showing Fawcett's ellipsoids. Dimensions in units of 10^8 cm.⁻¹.

$\phi = 0$, $\theta \sim 80^\circ$ (Fig. 3). In Fawcett's model, the ellipsoids which we have assigned to the [110] faces have a combined volume of 0.15 states per atom, and the remaining one 0.13 states per atom. Since tin has four valence electrons per atom, it is plausible to suppose that the first zone is completely filled, and that about 0.14 electrons per atom overlap from the second zone into the third. From anomalous skin effect measurements alone it cannot be decided which ellipsoids represent electrons and which holes; that is, whether overlap into the third zone occurs on the [110] faces, leaving holes on the [101] faces, or vice versa. Here magnetoresistance measurements might give useful guidance, and a theoretical band-structure calculation would also be of great interest; in particular, to decide whether the scheme suggested here is qualitatively plausible or not.³

The only other metal which has been studied experimentally so far is copper, on which Pippard (unpublished) has recently made a detailed series of measurements. Unfortunately his analysis of the results is not yet complete, but it may be said that the Fermi surface must depart considerably from spherical form, since the observed values of Σ_x vary over a range of 1 to 1.8.

It should be remarked that the d-c. conductivity of a sufficiently thin metal film (though not of a wire) is also determined primarily by electrons

³Unfortunately, it now seems doubtful whether the model shown in Fig. 4 is correct: in this model the minor axes of the two side ellipsoids are along the (110) directions, whereas Dr. Fawcett informs me that the minor axes of his ellipsoids are along the (100) directions, i.e. his ellipsoids differ from those shown here by a 45° rotation about the tetrad axis. This makes it much more difficult to fit them plausibly into the zone structure.

travelling at small angles to the surface, since they alone travel appreciable distances before colliding with the surface; thus the study of single-crystal thin films offers in principle an alternative method of obtaining the information gained from anomalous skin effect measurements. This problem has been studied theoretically by Kaganov and Azbel' (1954), who consider an arbitrary Fermi surface in the limit $l \gg d$, where d is the film thickness, and by Engelman and Sondheimer (1956), who consider spheroidal energy surfaces and give expressions valid for all ratios l/d . The expression obtained by Kaganov and Azbel' (slightly generalized) is

$$(13) \quad \sigma_{ik} = \frac{e^2 d}{4\pi^3 \hbar} \int_0^{2\pi} \frac{n_i n_k d\phi}{K(\frac{1}{2}\pi, \phi)} \ln \frac{l(\frac{1}{2}\pi, \phi)}{d}$$

where $n_x = \cos \phi$, $n_y = \sin \phi$. Thus apart from the logarithmic dependence on the mean free path of the small-angle electrons, this yields essentially the same quantity as Σ_x . In fact, however, this result is of purely academic interest: for any practicable film thickness, the localization of 'effective' electrons in \mathbf{k} -space is far less complete than in the anomalous skin effect, and the expression for σ will involve $K(\theta, \phi)$ over a wide range of θ , and not merely $K(\frac{1}{2}\pi, \phi)$. And if, for instance, we require that 90% of the current shall be carried by electrons for which $80^\circ < \theta < 100^\circ$ (for which we might hope that $K(\theta, \phi) \sim K(\frac{1}{2}\pi, \phi)$ so that (13) could be applied), it is easy to show that we require $d \sim 10^{-9}l$ —i.e. a film thickness of a fraction of an Ångström.

THE DE HAAS - VAN ALPHEN EFFECT

The de Haas - van Alphen effect—the oscillation of magnetic susceptibility with field exhibited by metals at low temperatures—is in principle far more powerful a tool for the study of metals than either of those so far discussed. It can yield, in favorable cases, detailed information about both the shape of the Fermi surface and the value of $dE/d\mathbf{k}$ at the surface, and this information is obtainable by application of an explicit inversion formula to the experimental results, rather than by a trial and error fitting procedure; it can also give some information about the relaxation time. As we shall see, however, the outlook is not quite so rosy as it would appear from this, and comparatively few detailed results are available so far. The theory has been discussed by Pippard (1955), and an excellent review of the whole topic by Shoenberg (1956) will appear shortly; we confine ourselves here to a brief sketch of the physical basis of the effect.

When a magnetic field H_z is applied to a free-electron metal, the motion in the z direction remains unquantized, so that k_z can have any value, but the motion in the x - y plane is quantized, so that for given k_z the total energy of an electron can assume only certain discrete values, which can be calculated by solution of the Schrödinger equation (cf., e.g., Dingle 1952a). For an electron moving in a lattice, a similar effect occurs, but here the solution of the Schrödinger equation is a much more difficult problem, and the whole theory of the de Haas - van Alphen effect in real metals is based on an ap-

proximate method of calculating the energy levels suggested by Onsager (1952). It is assumed, as in cyclotron resonance theory, that the motion of the electron is governed by the Lorentz equation (1), so that the electron follows an orbit in \mathbf{k} -space on the plane $k_z = \text{constant}$, and it is assumed that the allowed orbits are those which satisfy the Bohr-Sommerfeld quantization rule

$$(14) \quad \oint \mathbf{P} \cdot d\mathbf{r} = (n + \gamma)h$$

where n is integral, $0 < \gamma < 1$, and \mathbf{P} is the momentum variable conjugate to \mathbf{r} ; in the semiclassical approximation used here, $\mathbf{P} = \hbar\mathbf{k} + e\mathbf{A}/c$ where \mathbf{A} is the vector potential. Now as we have remarked, if an electron obeys equation (1) its motion in the x - y plane in real space is simply related to its motion in the k_x - k_y plane in \mathbf{k} -space; thus at any instant a simple relation exists between \mathbf{k} , \mathbf{r} , and $\mathbf{A}(\mathbf{r})$, and using this it is readily shown that (14) reduces to

$$(15) \quad \mathcal{A} = 2\pi(n + \gamma)eH/\hbar c$$

where \mathcal{A} is the area of the orbit in the plane $k_z = \text{constant}$, as before. The quantized values of the energy, for given k_z , will be those associated with the orbits permitted by (15); k_z itself remains unquantized and can have any value. For free electrons, this treatment gives the correct values for the energy if we take $\gamma = \frac{1}{2}$. Consider now the behavior of a free-electron metal at the absolute zero according to this model. In zero field the electrons occupy a sphere in \mathbf{k} -space with maximum energy E_0 . In a field H_z , they will lie on a series of cylinders about the k_z axis, with cross-sectional areas $\pi eH/\hbar c$, $3\pi eH/\hbar c$, \dots , as shown in Fig. 5. For given k_z , each permitted orbit is highly degenerate, and can accommodate all the electrons which would, in zero field, lie between it and the next permitted orbit. It thus turns out, in fact, that the maximum occupied energy, shown dashed in Fig. 5, is hardly altered

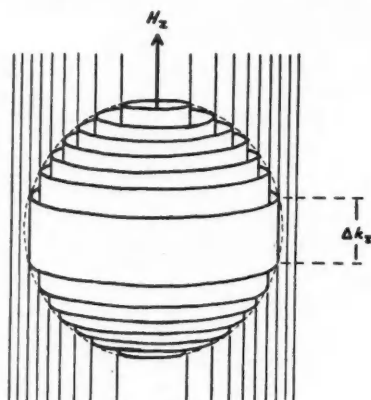


FIG. 5. Illustrating the origin of the de Haas - van Alphen effect.

from E_0 . The mean energy \bar{E} of all the electrons, on the other hand, shows appreciable oscillations about its zero-field value as H increases, and since the susceptibility $\chi = -d^2\bar{E}/dH^2$, it is this which gives rise to the oscillations in χ . It is clear from Fig. 5 what will determine the period of the oscillations. As H increases, the cylinders expand uniformly in area according to (15). For the inner cylinders this will lead, if anything, to a smooth variation of \bar{E} with H , but for the outermost occupied cylinder the occupied length, Δk_z , will shrink very rapidly as the area \mathcal{A} of the cylinder approaches the extremal cross-sectional area \mathcal{A}_0 of the Fermi surface, and at a critical field given by

$$(16) \quad 1/H = 2\pi(n+\gamma)e/\hbar c \mathcal{A}_0$$

(where n is the quantum number for this cylinder) it will become completely empty. As the field is further increased, this process will be repeated with the next inner cylinder, of quantum number $(n-1)$, and it is clear that the consequent oscillations in \bar{E} and therefore in χ will have a period

$$(17) \quad \Delta(1/H) = 2\pi e/\hbar c \mathcal{A}_0.$$

This is the central result of Onsager's treatment, and although we have deduced it by considering a free-electron model, it is equally valid for electrons in a lattice. The permitted energy surfaces are then tubes of complicated shape but constant cross-sectional area \mathcal{A} , running in the general direction of the k_z axis, and the oscillations of \bar{E} and χ are again caused by the expansion of the outermost tube through the Fermi surface, at the point where the cross-sectional area normal to H_z has its extremal value \mathcal{A}_0 . Consideration shows that if the Fermi surface is not a single closed convex surface, it may have a number of extremal areas for a given field direction (some of which may be minima, rather than maxima): all will then contribute independently to the oscillations of \bar{E} and χ , which may therefore show a complicated beat structure when plotted against $1/H$.

So far we have considered only conditions at the absolute zero. At finite temperatures, it is clear that the amplitude of the effect will be reduced: instead of all states up to energy E_0 being occupied, and all higher states empty, the density of occupation will now fall continuously to zero in a region of width $\sim kT$ around E_0 . If kT is comparable with or greater than the energy difference between successive quantized orbits in the region of \mathcal{A}_0 , the expansion of successive tubes through the blurred Fermi surface will produce only slight variations in \bar{E} , or in the free energy F (at finite temperatures, $\chi = -d^2F/dH^2$), and the de Haas-van Alphen effect will be greatly reduced in magnitude. The spacing between successive levels near \mathcal{A}_0 is given by

$$(18) \quad \Delta E = (dE/d\mathcal{A})_{\text{ext}} \Delta \mathcal{A} = (2\pi e H/\hbar c) (dE/d\mathcal{A})_{\text{ext}} = e H \hbar / m^* (\mathcal{A}_0) c$$

where m^* is the 'orbit mass' already encountered in considering cyclotron resonance (equation (3)). (We note incidentally that the condition $\omega = \omega_c$ for cyclotron resonance is, from this point of view, simply the condition $\hbar\omega = \Delta E$ for transitions between adjacent quantized orbits.) Thus we expect the amplitude of the oscillations to depend on the ratio $kT/\Delta E = kT m^* (\mathcal{A}_0) c / e H \hbar$. This is confirmed in the detailed evaluation of the Onsager

theory by Lifshitz and Kosevich (1954, 1955), following the treatment first given for the free-electron case by Landau (1939); they find for the oscillatory term in the free energy

$$(19) \quad F \propto T H^{3/2} \exp - [2\pi^2 k T m^* (\mathcal{A}_0) c / e H \hbar] \cos[(\hbar c \mathcal{A}_0 / e H) + \delta]$$

where δ is a constant phase angle, usually unimportant since $\hbar c \mathcal{A}_0 / e H = 2\pi n$ is usually large in reasonable fields.

So far we have also neglected the effect of collisions: these will broaden the energy levels by an amount $\sim \hbar/\tau$, and we may expect that this will also reduce the amplitude of oscillation unless $\hbar/\tau \ll \Delta E$, i.e. unless $\omega_c \tau \gg 1$ in the language of cyclotron resonance. Dingle (1952b) has shown that for free electrons the amplitude is reduced by collisions by a factor $\exp(-2\pi/\omega_c \tau) = \exp(-\hbar/\tau \Delta E)$, and we may expect the same result to hold for electrons in a lattice, with $1/\tau$ replaced by its mean value $(1/\tau)_{\text{ext}}$ around the extremal orbit. The effect of collisions is thus to increase the effective temperature in (19) by an amount

$$(20) \quad \Delta T = \hbar (1/\tau)_{\text{ext}} / 2\pi^2 k.$$

Thus by applying a magnetic field at various angles (θ, ϕ) to the crystal axes and measuring the period in $1/H$ of the de Haas - van Alphen effect, we can at once find from (19) the extremal areas $\mathcal{A}_0(\theta, \phi)$ of the Fermi surface normal to the directions (θ, ϕ) , and by observing the temperature-dependence of the effect at a given field we can also find, from (19), the values of m^* and hence of $(d\mathcal{A}_0/dE)_{\theta, \phi}$ at the extremal cross-sections. Note here that we measure in this way the value of m^* for one particular orbit, and not merely the average over the Fermi surface as in cyclotron resonance experiments. Lastly, from measurements of the field-dependence of the oscillation amplitude at a given temperature, we should be able to deduce the effective temperature $T + \Delta T$, and hence from (20) the value of $(1/\tau)_{\theta, \phi}$ around the extremal orbits.

The interpretation of these data is greatly simplified, in favorable cases, by an ingenious theorem due to Lifshitz and Pogorelov (1954). They assume that the Fermi surface is centrosymmetric and that the extremal section is always the central section (i.e. $k_z = 0$); with these assumptions they show that if the geometry of the surface is specified by the length $k_r(\theta_0, \phi_0)$ of the radius vector from the center to the surface in the direction (θ_0, ϕ_0) relative to the crystal axes, then $k_r^2(\theta_0, \phi_0)$ can be evaluated directly from a suitable average of $\mathcal{A}_0(\theta, \phi)$ over directions around (θ_0, ϕ_0) . Thus the determination of the shape of the surface from the experimental data is reduced simply to the application of their inversion formula. They have pointed out, moreover, that by differentiation $2k_r(dk_r/dE)$ can be evaluated, using the same formula, from measurements of $(d\mathcal{A}_0/dE)_{\theta, \phi}$. Knowing both $k_r(\theta, \phi)$ and $(dk_r/dE)_{\theta, \phi}$, we can at once evaluate $\hbar v_F$, that is, we can find the Fermi velocity and the density of states at all points on the Fermi surface. The de Haas - van

Alphen effect thus appears, in principle at least, to be a remarkably powerful tool for the study of metals.⁴

The experimental work on the de Haas - van Alphen effect falls into two groups: 'low-field' experiments, using conventional electromagnets at fields up to about 20 kG., and 'high-field' experiments (Shoenberg 1953, 1956), using an ingenious impulsive-field technique, up to about 100 kG. For the major parts of the Fermi surface in most metals, we might expect extremal areas \mathcal{A}_0 of the order of 10^{16} cm.²: from (17) we then find, for the period in H ,

$$\Delta H = H^2 \Delta(1/H) \sim 10^{-8} H^2,$$

where H is measured in gauss.

Thus in a field of 20 kG., $\Delta H \sim 4$ G. only, and detection of such short-period oscillations would be extremely difficult. Moreover if $m^* \sim m_0$, the free-electron mass, then at 1° K. the exponential term in (19) becomes approximately $\exp-(1.6 \times 10^5/H)$, i.e., at 20 kG., e^{-8} , so that the amplitude of the effect will be extremely small. Thus with low-field experiments we can only hope to detect Fermi surfaces for which \mathcal{A}_0 is very small, i.e. small pockets in the zone structure, containing very small numbers of electrons or holes per atom ($\sim 10^{-3}$ or less), and of rather small effective mass ($\lesssim 10^{-1} m_0$). Such small pockets appear to exist in a surprising number of metals (Shoenberg 1952, 1956), and for instance tin appears to have somewhere within the zone structure pockets containing about 2×10^{-3} electrons or holes per atom, in addition to the major surfaces discussed previously. Such small pockets can generally be treated as ellipsoids, which considerably simplifies the analysis of the experimental data; where values of m^* have been deduced from the temperature-variation of the effect, their behavior also agrees well with the ellipsoidal model. Except in one or two cases, however, the low-field results are of relatively little interest, because these small pockets have little effect on the general properties of the metal compared with other, much larger, regions of the Fermi surface which are not detected by low-field experiments. The exceptional cases are the semi-metals, As, Sb, Bi, and C (graphite), in which it seems that the small pockets found experimentally do indeed form the major part of the Fermi surface. Bismuth, in which the de Haas - van Alphen effect was first discovered, has been particularly closely studied by Shoenberg and others; the results correspond to three ellipsoids containing altogether 1.5×10^{-5} electrons per atom which overlap into the second zone, and it seems that these electrons, together with the corresponding holes in the first zone,

⁴It may be noted that the same basic theorem of Lifshitz and Pogorelov, applied to anomalous skin effect measurements of $(\Sigma_x^2 + \Sigma_y^2)$, enables us to evaluate directly the Gaussian curvature $K(\theta_0, \phi_0)$ at any point on the Fermi surface, where θ_0, ϕ_0 now specify the direction of the normal to the Fermi surface at that point. This is, however, hardly so direct a description of the Fermi surface as that considered above. Their theorem cannot be used, incidentally, to find $1/r$ at the point (θ_0, ϕ_0) from the mean values $(1/r)_{\theta, \phi}$, because the average involved in $(1/r)$ is not over a true angle variable in \mathbf{k} -space, but over the fictitious 'orbit angle' introduced by Shockley (1950): this is related to a true angle in \mathbf{k} -space, but only rather indirectly.

constitute the whole Fermi surface of Bi; for instance, the same model has been shown by Abeles and Meiboom (1956) to account quite well for the magneto-resistance properties. Heine (1956a) has suggested that the holes left in the first zone show no de Haas - van Alphen effect because of their high effective mass, and has shown that the model can account quite plausibly for most of the observed properties of Bi. The case of graphite is particularly interesting: if an attempt is made to fit the results to an ellipsoidal model, the resultant ellipsoid turns out to be extremely elongated in the direction of the hexagonal axis; so much so that its length exceeds the space available in the reduced zone. We shall return to this point later.

The only metal so far which has been examined in any detail on the basis of the Onsager-Lifshitz theory is aluminum. Here low-field oscillations are readily observable which cannot be fitted to an ellipsoidal model, and Gunnerson (1956) has carried out a detailed experimental survey and has analyzed the results using the formula of Lifshitz and Pogorelov. The analysis indicates a set of 'cushion-shaped' surfaces, containing altogether about 3.6×10^{-3} states per atom. Because of the presence of three separate periods in the experimental data, it is difficult to determine their individual amplitudes accurately, and consequently a detailed analysis of m^* has not been attempted. By combining the information obtained from Gunnerson's results with the evidence from specific heat data and from anomalous skin effect measurements on polycrystalline material, Heine (1956b) has been able to arrive at a reasonably complete picture of the Fermi surface in aluminum, using as his basic guide a detailed calculation of the band-structure by the O.P.W. method. He concludes that the 'cushion-shaped' surfaces found by Gunnerson are formed by holes at the corners of the first zone, which is almost completely filled, as shown in Fig. 6. The remaining electron overlaps into the second zone across all faces, as shown in Fig. 7, and there is probably also a very slight overlap into the third zone at points near the corners: this may account for a very low-frequency period observed but not analyzed by Gunnerson. Heine has not been able to decide from the evidence available whether the second

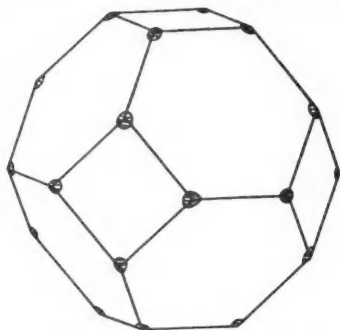


FIG. 6. The first zone in aluminum according to Heine (1956b).

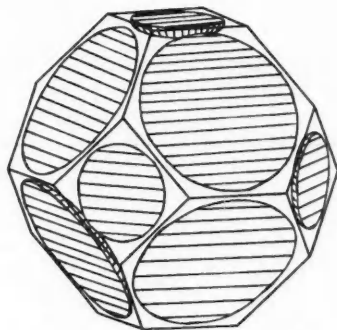


FIG. 7. The second zone in aluminum, according to Heine (1956b).

zone is in fact as shown in Fig. 7, or whether the filled regions link together across the mid-points of the zone edges, to form a single surface with gaps at the zone corners. This possibility introduces a basic complication in Fermi surface geometry which we have so far largely ignored.

If the Fermi surfaces in aluminum have the forms shown in Figs. 6 and 7, it is possible to remap them into a set of closed, simply-connected surfaces, each of which can then be considered separately by the methods so far described, and this is always possible if the separate sections of the Fermi surface in the reduced zone are localized on separate zone faces or around separate corners. But if the sections of the Fermi surface extend from one zone face to the next, or from one corner to the next, such a remapping is no longer possible, and the Fermi surface is then essentially multiply connected. The simplest example of this appears to be graphite, where the experimental results described above suggest that the Fermi surface is a tube extending right across the zone from one face to the opposite face (Onsager 1952, 1955). The situation in for instance a cubic metal will be much more complicated than this, however: if one thinks of the reduced zone as repeated periodically throughout \mathbf{k} -space, the multiply-connected Fermi surface will form a complex three-dimensional network whose structure and properties it is very difficult to visualize. Such structures may well occur quite often in multivalent metals, however, and it is important to consider how far the methods of analysis described so far will apply to them. We may note first that if the magnetic field is applied in a direction perpendicular to a reciprocal lattice vector, there may exist 'open' orbits which pass from a point A_1 on one zone face to the equivalent point A_2 on the opposite face, and so extend indefinitely through \mathbf{k} -space. The existence of such orbits is easily visualized in the case of graphite, where the Fermi surface itself is simply a tube extending indefinitely through \mathbf{k} -space; they may also arise in cubic metals, and Fig. 8 attempts to depict

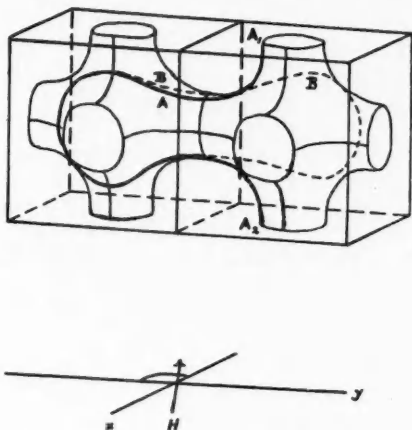


FIG. 8. Illustrating open and extended orbits in a simple cubic lattice.

such an orbit A_1AA_2 for a simple cubic lattice, with the field H in the x - y plane. It will be seen that the orbit passes out of one cycle of the reduced zone and into the next on its way from A_1 to A_2 . Also shown, as a further complication, is an 'extended' orbit BB , which closes only after passing through two cycles of the reciprocal lattice. Now the orbit BB is a closed orbit, and will presumably still have a definite quantized energy and area, and the Onsager quantization condition (15) should still be applicable to it; it is also an extremal area and should therefore be observed experimentally. It is not difficult to see from Fig. 8 how the oscillation period associated with such an orbit will vary with field direction, and for a simple cubic lattice the interpretation of the observations might present no great difficulties, but if such orbits are ever observed experimentally in real b.c.c. or f.c.c. metals, where the situation may be much more complex, their interpretation will be an interesting exercise in three-dimensional visualization. Returning now to the open orbit A_1AA_2 , it is clear that since this orbit never closes, the Onsager quantization condition cannot be applied, and in fact such an orbit is almost certainly not quantized at all, and so can give rise to no observable de Haas - van Alphen effect. Now consider what happens when the magnetic field is tilted slightly out of the x - y plane. The point A_2 will then no longer be exactly equivalent to the point A_1 , so that the path through the next pair of zones, beneath those shown, will not be an exact repetition of A_1AA_2 , and in fact consideration shows that the orbit will now be an extremely tortuous curve in \mathbf{k} -space, which returns to the point A_1 , if at all, only after travelling a great distance, during which it will have covered a large part of the accessible Fermi surface (cf. Shockley 1950). Such an orbit may appropriately be called 'quasi-ergodic': clearly, even if it does eventually close, the associated frequency ω_c will be extremely low, so that $\omega_c\tau \ll 1$ and again no de Haas - van Alphen effect (or cyclotron resonance effect) can arise from such an orbit.

It is clear, therefore, that if the Fermi surface is multiply connected considerable complications can arise in the interpretation of de Haas - van Alphen effect measurements or cyclotron resonance measurements, and under these conditions the anomalous skin effect may prove a simpler tool to use. Nevertheless, we should certainly not expect the de Haas - van Alphen effect to be suppressed completely because of these complications, and it is therefore puzzling that the high-field experiments, which we have not so far considered, show no further oscillations in aluminum, for instance, beyond those already found by Gunnarsen: there is no sign of the effects which might be expected from the electrons in the second zone. The high-field method has indeed revealed oscillations in Pb, of such a frequency that they are probably associated with the main part of the Fermi surface, and these are at present being investigated in detail by Mr. A. V. Gold in the Mond laboratory, and high-frequency oscillations have also been found in tin and a few other complex metals; those found in tin have not yet received systematic study, but it seems probable that they too arise from the main part of the Fermi surface, and it is very desirable that a full study should be made for comparison with Fawcett's anomalous skin effect results.

It is particularly puzzling and disappointing that no oscillations have yet been found in the group I metals Li, Na, Cu, Ag, Au at any field up to 100 kG., although theoretical calculation suggests that oscillations should be readily observable by the high-field method. Unless this failure is due to some unsuspected weakness in the experimental technique, it seems to suggest the presence of some effect which is not taken account of in the Onsager-Lifshitz theory. An indication of what this effect might be is provided by the results of measurements on the field-dependence of amplitude. From these, as we have seen, it should be possible to obtain the value of the mean relaxation rate $(1/\tau)$. In fact Shoenberg (1952) has found that for a number of metals $(1/\tau)$, so deduced, is about a hundred times greater than the expected value, although the increase in $(1/\tau)$ on adding impurity to the metal agrees well with expectation. Now we have already remarked that magnetoresistance measurements in a high field H_z indicate a conductivity σ_{xx} proportional to $|H|^{-1}$, and this would be accounted for if $(1/\tau)$ increased with $|H|$, for instance because of field-dependent scattering by dislocations; it may be that Shoenberg's results have a similar explanation, but from the magnitude of the discrepancy he finds, this seems improbable. Alternatively, it may be that in fact the energy levels have an intrinsic breadth, over and above that caused by collision broadening, and Dingle has suggested that this intrinsic breadth might be an effect due to the lattice potential. Such a broadening is not taken into account at all in the Onsager theory; if, for some reason, it is particularly large in the group I metals, it will account for the failure to observe oscillations in them, and moreover it seems probable that cyclotron resonance effects will be similarly suppressed.

Before discussing this possibility in detail we may remark on a discrepancy which exists between the expressions for the *steady* diamagnetism of a metal according to the Onsager theory and according to Peierls's (1933) exact theory. Using the notation of equations (1)–(4), the result obtained by Peierls can be put in the form (for a closed Fermi surface):

$$(21) \quad \chi = -(e^2/48\pi^3c^2) \int dk_z \oint_{E_0} dk_t / \rho m_n$$

where ρ is the radius of curvature of the orbit (E_0, k_z) at point k_t , and $m_n^{-1} = \hbar^{-2} d^2 E / dk_n^2$; the integration extends over all k_z for which orbits of energy E_0 exist. If we take $\gamma = \frac{1}{2}$ in equation (15), and evaluate χ in the usual way by using the Euler summation formula, Onsager's approach yields

$$(22) \quad \chi = -(e^2/48\pi^3c^2) \int dk_z 2\pi/m_0^*$$

where m_0^* is the value of $m^*(\mathcal{A}, k_z)$ for $\mathcal{A} \rightarrow 0$; the integration over k_z extends over the same limits as in (21). A similar expression has been obtained for arbitrary γ by Lifshitz and Kosevich (1955), using the Poisson summation formula. Now for spherical or ellipsoidal Fermi surfaces, (21) and (22) yield identical results for χ , and indeed for these cases it is well known that a semiclassical treatment gives correct results (Mott and Jones 1936), but in general they do not, and it is difficult to see how agreement could be restored

by supposing, for instance, that $\gamma = \gamma(n)$. This discrepancy may possibly be the result of level broadening, which is neglected in the Onsager theory but is implicitly taken into account in Peierls's treatment.

A theoretical study of level broadening involves an attack on the difficult problem which the Onsager treatment was designed to avoid: the solution of the Schrödinger equation for an electron moving through a lattice in a magnetic field. This problem may be tackled at two levels of difficulty: if we assume that the solution wave-function, for an electron in a given zone, can be expressed in terms of the zero-field wave-functions (e.g. Bloch functions or Wannier functions) from the same zone only, the problem is considerably simplified, but the solution will still be inexact; alternatively we can attempt to find the exact solution, including the contribution to the wave-function from states in other zones—the non-diagonal or 'inter-band mixing' terms—and the problem then becomes extremely complicated. If the non-diagonal terms are neglected, the energy levels can in principle be found from Peierls' (1933) form of the Hamiltonian: if $E = E(\mathbf{k})$ gives the energies in $H = 0$, then according to Peierls the energies in a field H are given by the solution of the equation $E = E(\kappa)$, where κ is now an operator whose components obey $[\kappa_x, \kappa_y] = ieH_z/\hbar c$, etc. Adams (1952) has shown how this equation must be generalized to take account of the non-diagonal terms, and has succeeded in showing (Adams 1953) that their effect on the steady diamagnetism is extremely complicated and may be quite large if the energy gap between zones is small; he has not however considered their effect on the individual energy levels. Luttinger and Kohn (1955; see also Luttinger 1956) have considered this effect, with reference to cyclotron resonance in Ge and Si, but they restrict themselves to forms of $E(\mathbf{k})$ which involve terms not higher than k_z^2 , etc.; their result is in the form of a complicated set of coupled differential equations. Harper (1955*b*) has also studied this problem, for a rather different form of $E(\mathbf{k})$, and concludes that the effect of non-diagonal terms on the level spacing and level broadening will be small unless the energy gap between zones is small; what effect will occur when the gap is small is not clear from his treatment. He has also considered (Harper 1955*a*) the simpler problem which arises if the non-diagonal terms are omitted, using for this purpose Peierls's form of the Hamiltonian: this is only practicable if $E(\mathbf{k})$ is chosen to have rather simple form, and Harper considered a simple cubic lattice in the tight binding approximation, for which $E(\mathbf{k}) = -E_1(\cos k_x a + \cos k_y a + \cos k_z a)$, in an applied field H_z . He found that the energy levels for given k_z were considerably broadened near $E = -E_1 \cos k_x a = E_c$ say; i.e. near $\cos k_x a + \cos k_y a = 0$, or $\pm k_x \pm k_y = \pi/a$. According to Harper, the broadening was appreciable over a wide range of energies around E_c , but Brailsford (1956) has re-examined the problem and finds that in fact the broadening is only appreciable extremely close to $E = E_c$. Brailsford has also remarked that the energy levels, neglecting broadening, are identical with those given by the Onsager treatment. Now on the Onsager treatment, the orbits of energy E_c are precisely those for which broadening might be expected: Fig. 9 shows the orbits corresponding to the Harper-Brailsford model, for constant k_z , and it

so that at $x = y = 0$, $H_z = H_0$. If we insert this expression for \mathbf{A} in the Schrödinger equation, and express the solution wave-functions in the form

$$(24) \quad \psi = \sum_n \int d\mathbf{k} a_{n,\mathbf{k}} \psi_{n,\mathbf{k}},$$

where the integration extends over the reduced zone, it is a straightforward matter to derive a differential equation for the coefficients $a_{n,\mathbf{k}}$ in the limit $L \rightarrow \infty$; moreover it is easy to show that if instead of (23) we take more generally

$$\mathbf{A} = H_0 L (\sum b_n \sin 2\pi n y / L, -\sum b_n \sin 2\pi n x / L, 0) / 4\pi \sum n b_n,$$

the equation for $a_{n,\mathbf{k}}$ is unchanged; physically, because the wave-function ψ is localized around $x = y = 0$, in the uniform field $H_z = H_0$.

The general equation including non-diagonal terms need not be given here: it is closely similar to an equation derived but not discussed by Harper (1955*b*, eq. 2.4), though the present derivation seems more direct and physically simpler. If we neglect non-diagonal terms, the equation becomes simply a differential equation for $a_{\mathbf{k}}$ within a single band:

$$(25) \quad \frac{ieH_0}{2c} \left(v_y \frac{\partial a_{\mathbf{k}}}{\partial k_x} - v_x \frac{\partial a_{\mathbf{k}}}{\partial k_y} \right) - \frac{e^2 H_0^2}{8mc^2} \left(\frac{\partial^2 a_{\mathbf{k}}}{\partial k_x^2} + \frac{\partial^2 a_{\mathbf{k}}}{\partial k_y^2} \right) = (E - E_{\mathbf{k}}) a_{\mathbf{k}}$$

where E is the energy of the state ψ . For free electrons equation (25) for $a_{\mathbf{k}}$ becomes mathematically identical with the corresponding equation for $\psi(\mathbf{r})$, the solutions of which have been discussed by van Vleck (1932) and Dingle (1952*a*): it can be shown that in this case the solutions $a_{\mathbf{k}}$ are simply the Fourier transforms of the solutions $\psi(\mathbf{r})$, as of course they should be.

Equation (25) does not contain k_z explicitly, corresponding to the fact that k_z is a constant of the motion, and the solutions will thus exist on planes $k_z = \text{constant}$; the boundary condition is that $a_{\mathbf{k}}$ shall be continuous throughout the plane. In the free-electron case, there is an infinity of solutions for given energy having different values of the quantum number l , where $a_{\mathbf{k}}$ varies with azimuth angle ϕ about the point $k_x = k_y = 0$ as $\exp(\pm il\phi)$, and (25) will similarly have an infinity of solutions if the above boundary condition is not imposed; on imposing it, however, only the $l = 0$ solution survives, and for this solution the wave-function $a_{\mathbf{k}}$ corresponding to a given semiclassical orbit in \mathbf{k} -space is non-zero and oscillatory within that orbit, and falls off exponentially rapidly outside it. It now becomes clear when level broadening is to be expected. Consider for instance the situation shown in Fig. 9. If we consider a state with energy small compared with E_c , for which the semiclassical orbits are small circles about the center of each cell in the plane (as shown shaded), the corresponding wave-functions will be localized within these circles and will overlap with each other to a quite negligible extent: the energy will be sharply defined and will correspond to that given by the Onsager treatment. Now consider what happens as E approaches E_c . The semiclassical orbits expand and approach those in neighboring cells, and correspondingly the $a_{\mathbf{k}}$ functions will overlap one another to a gradually increasing extent. The situation may be compared with that which arises when a solid is formed by bringing its constituent atoms closer and closer together: in that

case the energy levels of the valence electrons are well defined and equal until their wave-functions begin to overlap, and they then broaden out into a band, whose breadth depends on the degree of overlap. An exactly similar effect will occur in the present case: the overlap and the broadening remain extremely small until the energy is very close to E_c , because of the rapid falling-off of a_k outside the classical orbit, but in the immediate neighborhood of E_c the overlap and the broadening will be considerable. It might appear that the broadening would be still greater for $E > E_c$, but if we now use 'hole' wave-functions instead of electron wave-functions, a_k will again be localized inside the semiclassical orbits about the corners of the zones, and the spreading will again be small.

We have considered the argument in detail here only for a special $E(\mathbf{k})$ and a special field direction; it can be applied equally well, however, to more general cases, and it is clear that the only region in which appreciable level broadening is to be expected is in the immediate neighborhood of the semiclassical open orbits, and for instance the 'extended' orbits previously considered should have, as we conjectured, well-defined energy levels.

We have already seen, on the semiclassical picture, that no de Haas - van Alphen effect is to be expected from open orbits, and thus level broadening does not materially alter the situation. In particular, it seems improbable that it can explain the absence of a de Haas - van Alphen effect in the group I metals, unless the broadening due to non-diagonal terms is unusually large in these metals, which seems improbable. It may be that the failure to observe the effect is due after all to experimental difficulties, and it seems well worth while to continue the search: accurate information on the energy levels in these metals, if it could be obtained, would be of great theoretical interest.

I am indebted to Dr. Shoenberg, Dr. Pippard, Dr. Fawcett, and Messrs. Brailsford, Gunnensen, and Heine for informing me of their work before publication.

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DISCUSSION OF CHAMBERS'S PAPER

Kubo: Can you say what was the orientation of Fawcett's tin specimen?

Chambers: I can't remember, but it is given in Fawcett's letter to *Physical Review*.

Pearson: I wish to point out that additional information may be gained by changing electron concentration in solid solution by alloying, and this could be used for checking effects like those in tin or bismuth. One might also mention the earlier work on magnesium alloys in which particular lattice spacing changes vary with electron concentration; this was interpreted in terms of overlap of specific faces of the Brillouin zone.

Chambers: This is a good point, but there are experimental difficulties. A pure metal is essential for cyclotron resonance ($\omega\tau$ large) and for the anomalous skin effect (mean free path large compared with δ). A reasonably pure metal is also needed for the de Haas - van Alphen effect, but it can still be seen at a moderate impurity content: experiments on bismuth alloys, for instance, verify that here the de Haas - van Alphen effect is due to electrons, and not holes. Alloying was also tried by Gunnensen in aluminum, but there was no appreciable change in the period of the effect for the concentrations

tried and we cannot tell therefore whether electrons or holes are responsible: according to Heine's theory it is holes.

Ziman: I think you could get quite a lot of information from good experimental work on magnetoresistance of a single crystal. What has been done here?

Chambers: This is indeed important. Before the war there were available only a few observations on gold by Justi, and a systematic study of beryllium by Grüneisen and his colleagues—and beryllium is a most complicated metal. These experiments showed enormous anisotropy at low temperatures.

Since the war there has been some work at the N.R.L. on bismuth and also in Russia by Borovik on several metals. One would like to see similar work done on group I metals, and I believe that this has been started at Berkeley.

Gerritsen: There is also the work of Justi and Scheffers on copper and cadmium, of de Haas and Schubnikow on bismuth, and of de Haas and Blom on gallium, all before the war.

Algrain: We have been able to make thin films of n -type germanium in which the thickness was much smaller than the bulk mean free path, by taking the n -layer of a p - n - p sample.

Mott: It seems that the de Haas—van Alphen experiments give us lots of almost indigestible information about complex solids, but can tell us almost nothing about simple group I metals.

Sondheimer: What characteristic parameters are found for the more complex metals?

Chambers: 0.1 to 0.3 electrons per atom, with $m^* \sim 1$.

Slater: It is rather sad that most metallurgists know nothing about all the recent developments, but still rely implicitly on what Jones did twenty years ago. Can nothing be done about this?

Anon: Professor Slater should write a book.

Korringa: Well, most metal physicists know nothing about phase diagrams.

Mott: In fact the work of Heine has indicated that the electrons behave surprisingly like free electrons, so that their faith in Jones is justified in practice. And since the war we haven't got far enough on our new tack to tell the metallurgists anything useful.

Pearson: Most metallurgists never undergo an honors course in physics, and there is a real problem of interpretation. Dr. Hume-Rothery has done much to bridge the gap, but the process must be continued.

Klemens: It is possible to draw some conclusions about the shape of the Fermi surface in metals from their electrical and thermal conductivities, even though these quantities describe only an average behavior over the Fermi surface. In the case of electrical conduction the resistive processes must move an electron from a point on the Fermi surface to an opposite point, while in the case of thermal conduction there is, in addition to this process, the possibility of changing the energy of an electron by an amount of order kT . At low temperatures thermal resistance is due to the latter process, which is essentially a single step process, but the change of direction, responsible for

electrical resistance, is a process of diffusion over the Fermi surface, proceeding in many small steps.

If we assume a spherical Fermi surface, then the solutions of the Bloch equations for electrical and thermal conduction give us the effective relaxation times for both these processes, and in particular the ratio for these relaxation times. If the Fermi surface departs from spherical shape, we would expect the relaxation time for thermal resistance to be practically unaffected, being determined by a local phenomenon on the Fermi surface; on the other hand the relaxation time for electrical resistance, being determined by diffusion over the Fermi surface, should be sensitive to the shape of the Fermi surface.

If in particular the Fermi surface approaches the zone boundary sufficiently closely to allow Umklapp processes at low temperatures, this would result in substantial increase of the ratio of electrical to thermal resistance over the values calculated from the Bloch theory, since the path length of electrons diffusing over the Fermi surface is then considerably shortened. We would expect this to happen more easily for noble metals (face centered) than for alkali metals (body centered), for in the former case the zone boundaries come closer to the center of the zone; however, if the effect occurs in alkali metals the change of electrical resistance should be larger, because there are more points of closest approach for the body centered metals.

For the noble metals, the ratio of the low temperature electrical resistance to the thermal resistance does indeed exceed the theoretical value by a factor of about 5. For the heavy alkali metals there is a discrepancy of the order of 10, while for sodium the discrepancy is only about 2. This indicates that Umklapp processes do short-circuit the diffusion over the Fermi surface for the noble and the heavy alkali metals, but not for sodium.

The question arises whether the Fermi surface touches the zone boundary in these metals, or merely approaches it closely. In the latter case, Umklapp processes should be frozen out at a finite temperature, producing a deviation from the T^5 variation for electrical resistance. Work on purer specimens would throw light on this question. It is possible to put an upper limit on the distance of closest approach of the Fermi surface, though no quantitative work has yet been done on this. It appears certain, however, that the Fermi surface of the noble metals, even if it were not to touch the zone boundary, would have to come close to it, so that it must depart strongly from spherical shape.

In the case of sodium there is a departure from T^5 variation. It may be that this is due to the phonon drag effect discussed by Dr. Sondheimer at this conference.

MacDonald: I would like to reinforce Dr. Chamber's remarks about magnetoresistance in metals. I think there is no doubt that magnetoresistive measurements embody a great deal of potential information about conduction electron properties particularly when we can achieve large values of l/R , where l is the electron mean free path and R the orbital radius of a free electron in the applied magnetic field. Magnetoresistance is certainly also a bulk phenomenon, not depending on any special surface treatment of the metal.

However, theory is undoubtedly far from adequate in metals and surely offers a real challenge to theorists in view of the considerable wealth of experimental data available. Let me also say that in sodium (cf. MacDonald, *Handb. Physik*, **14**, 137 (1956)), generally regarded as a considerably closer approach to the free-electron model than even the noble metals, the magnetoresistance also varies as $|H|^{-1}$ (with no sign of saturation) after the initial rather complicated variation in "low" fields.

Perhaps I should mention as well that some years ago in Oxford I made some attempts at magnetoresistance measurements in liquid helium and hydrogen on *single crystals* of pure alkali metals; the specimens were cast in narrow glass capillaries. I had a modicum of success in getting something like single crystals of sodium (Dr. Pitt, Oxford, kindly made a number of X-ray measurements), but any anisotropy I observed was relatively small, compared with that in a metal such as tin. On the other hand I was unable to make satisfactory single crystals of rubidium or cesium in the glass capillaries. This was disappointing: one might expect results on these heavier alkali metals to be more interesting.

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